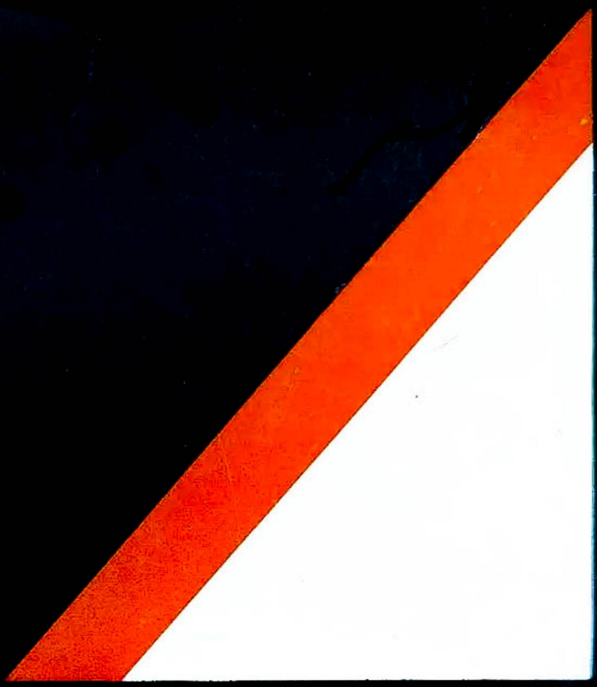

ENGINEERING THERMODYNAMICS AND HEAT TRANSFER

by V. Nashchokin

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ENGINEERING THERMODYNAMICS AND HEAT TRANSFER

Engineering Thermodynamics and Heat Transfer
is a textbook for college
and university students.
It will also be helpful to
engineers and technicians
working in the field
of power generation.
The first part discusses the laws
of thermodynamics, thermodynamic
processes and cycles of heat engines.
Internal combustion engines,
gas and steam turbines,
atomic power stations,
distinct heating stations,
refrigeration plants
and magneto-hydrodynamic
installations are then
analyzed in an applied section.
The second part discusses
the fundamentals of heat
transfer by conduction,
convection and radiation,
and the theorems
of similarity.
Insulation and the design of heat
apparatus are also discussed,
as well as heat and mass transfer
in moist bodies.
Problems are given with full solutions,
while to each chapter
of the book there are
review questions to assist
the student.
This text, widely used
by Soviet students,
has recently
gone into its 3rd Russian
edition in Moscow.

ENGINEERING THERMODYNAMICS AND HEAT TRANSFER

ИЗДАТЕЛЬСТВО
МИР

ПРОФ. В. В. НАЩОКИН

ТЕХНИЧЕСКАЯ ТЕРМОДИНАМИКА И ТЕПЛОПЕРЕДАЧА

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА»

V. V. NASHCHOKIN

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PREFACE

This book is intended as a textbook in energetics for non-specialist students in technical colleges and universities.

It aims to give a systematic presentation of the main problems of engineering thermodynamics and heat transfer in a single volume, in order to facilitate independent study of the subjects by students.

For students not specializing in energetics heat engineering is a general engineering subject which rightfully occupies a central place in the theoretical training of specialists.

With the development of electrification the importance of heat engineering is increasing all over the world.

The operation of high-power steam turbine plants, in electric stations with high-temperature and high-pressure steam;

the introduction of plants operated on binary cycles involving simultaneous use of both steam and the products of combustion of various fuels as working media;

the introduction of district-heating systems;

the development of jet engines and gas-turbine plants;

the widespread use of internal combustion engines in all fields of contemporary engineering;

the utilization of the enormous heat fluxes rejected from nuclear reactors to generate electric power, large-scale construction of food and chemical enterprises where fuel combustion products and steam serve as heat-carrying agents;

the introduction to industry of the magnetohydrodynamic method, permitting direct conversion of heat into electric power;

the use of refrigeration in industry and every-day life. Many problems raised by contemporary science and engineering have widened in an extraordinary way the scope of heat engineering and continuously have set before it new and important problems.

The first part of the book treats in detail the main laws of thermodynamics, thermodynamic processes, the differential equations of thermodynamics and the flow of gases and vapours through nozzles. The cycles of internal combustion engines, gas-turbine plants and steam turbines, the cycles of atomic power stations, district heating systems, direct-conversion MHD generators and refrigerating installations are considered also in a section on applications.

The second part of the book presents the laws governing steady-state and transient conduction, the theoretical fundamentals of similarity, convective heat transfer, thermal radiation heat transfer, and also the calculation principles for heat-exchange equipment. This part also includes data on heat and mass transfer in moist colloidal, capillary bodies.

Given at the end of each chapter are typical questions and numerical problems, taken from engineering practice. The SI system of units is used in the book.

Writing the textbook the author endeavoured to give a simple and understandable presentation of thermodynamics and heat transfer, while presenting the material in the required theoretical and scientific manner.

PART I

ENGINEERING THERMODYNAMICS

CHAPTER ONE

INTRODUCTION

1-1. Engineering Thermodynamics and Heat Transfer

Engineering thermodynamics and heat transfer are the most important subjects of contemporary energetics.

These subjects study the problems involved in the conversion of heat into work and the transfer of heat between bodies, into heat and refrigeration installations.

The science of thermal processes originated in the 19th century, and resulted from the study and theoretical justification of the performance of steam engines which found wide application in the 19th century. But the low efficiency of these engines has necessitated the creation of new machines such as steam turbines, internal combustion engines and gas-turbine plants, and these have been developed enormously in the last few decades to a high degree of perfection.

Electric power is generated all over the world in thermal electric power stations by the combustion of firing coal, oil or gaseous fuel. The importance of these chemical fuels in power engineering shall continue to be predominant for a long time.

Atomic power engineering will be greatly developed, and it tries to take a deserved place in the electric energy production. On January 1, 1976 the capacity of atomic power plants reached 80×10^6 kW, and by 1980 the capacity of all atomic power plants is expected to be 300×10^6 kW. The enormous growth of atomic power engineering is associated with the abrupt increase of chemical fuel consumption and the depletion of coal and oil reserves.

The new sources of electric energy also include the combustion of a mixture of deuterium and tritium (radioactive hydrogen isotopes), permitting generation of great amounts of electric power with minimal consumption of radioactive substances. Methods using deuterium alone are being developed, and the reserves of this isotope are practically inexhaustible.

The magnetohydrodynamic or direct-energy conversion method of electric energy utilizing the energy of plasma will be mastered. Plants with MHD generators, free of moving parts, can be operated with a 50 to 60 per cent efficiency, instead of the 35 to 40 per cent efficiency at the best thermal electric power stations.

Steam boilers will be designed to operate using steam at temperatures up to 600 °C and pressures of 300 bar and higher, and the capacity of individual boiler turbine units will be raised, contributing to a higher efficiency. Gas-turbine plants will find wide application.

High-temperature thermoelectric semiconductor generators and thermionic converters are being created, enabling the direct conversion of heat into electric power with an efficiency up to 15-20 per cent.

The problem of direct conversion of the chemical energy of fuel into electric power is being solved, and the appearance of new current sources and electrochemical energy generators can be expected. The first pilot-type electrochemical generators operating on gaseous hydrogen and oxygen have already been created in many countries. They corroborate the high effectiveness of direct conversion of the chemical energy of fuel into electric power with an efficiency reaching 80 per cent which exceeds considerably the efficiency of presently operated conventional power plants.

Solar energy will find wide application in the near future and heat from underground hot springs, in small-capacity plants. These can be used to distil salt water for agricultural purposes, heat water for everyday needs, dry fruits, heat buildings and so on. Sufficiently reliable plants of this kind have already been built and activities in this field will continue.

The expected extensive development of heat-and-power engineering poses huge problems for engineering thermodynamics, such as the investigation of the thermo-physical properties of water and steam at supercritical pressures up to 2000 bar and steam temperatures up to 1000 °C. These investigative methods can also be used to determine the thermo-physical properties of other working media which will find application in new atomic and thermal electric power stations, and in the chemical industry and elsewhere.

Carbon dioxide will be investigated over a wide range of pressures and temperatures.

Studies associated with heat pumps and refrigeration will be widely developed, as will be the peaceful uses of thermonuclear energy.

All the problems mentioned above for which engineering thermodynamics is of crucial importance indicate the paramount importance of the theoretical fundamentals of heat engineering.

1-2. Engineering Thermodynamics and Its Problems

Thermodynamics, being a division of theoretical physics, represents one of the widest fields of natural science, the science of conversion of various kinds of energy into one another. This science treats the most diverse natural phenomena and embraces a vast field of chemical, mechanical and physicochemical phenomena.

At the present time thermodynamics can be subdivided into three parts:

general, or physical, *thermodynamics*, studying the processes of energy conversion in solid, liquid and gaseous bodies, radiation from various bodies, magnetic and electrical phenomena; general thermodynamics also relates mathematically various thermodynamic quantities;

chemical thermodynamics, based on the laws of general thermodynamics, studies chemical, thermal (heat), physicochemical processes, equilibrium and how equilibrium is effected by environmental conditions (surroundings);

engineering thermodynamics, treating the laws governing processes involving mutual conversion of heat and work. It interrelates thermal, mechanical and chemical processes taking place in heat engines and refrigerating machines, studies processes occuring in gases and vapours, and also the properties of these bodies under various physical conditions.

Thermodynamics is based on two fundamental laws, generally known as the laws of thermodynamics.

The first law of thermodynamics involves application of the general law of Nature, the law of conservation and conversion of energy, to thermal phenomena.

The second law of thermodynamics establishes the direction of and the conditions under which macroscopic processes occur in systems composed of a large number of particles. That is why the second law of thermodynamics is not so widely applicable as the first law.

At the beginning of the 20th century one more empirical assumption was added to the two laws of thermodynamics, the so-called Nernst's heat theorem which makes it possible to determine the properties of bodies at very low temperatures. This theorem is mainly used in chemical thermodynamics and is of limited applicability.

The development of engineering thermodynamics dates back to the twenties of the last century, but, in spite of its being comparatively new, at the present time this field of science rightly occupies one of the central places among physical and engineering subjects.

From theoretical point of view engineering thermodynamics is a general branch of the science of energy and, as far as practical application is concerned, engineering thermodynamics is the theoretical foundation of heat engineering studying the processes occurring in heat engines.

Thermodinamics makes use of two methods of investigation: the method of cyclic processes and the method of thermodynamic functions and geometrical diagrams. The latter method of investigation, elaborated and described by Gibbs, has found wide application in the last few years.

At the beginning of second half of the 18th century a very important engineering problem was solved when a universal heat engine was created for industrial and transport usage. The first steam engine was designed, built and tested by the Russian engineer and scientist I. I. Polzunov. It was put into operation after his death in 1766 by his pupils at the Altai plants, i.e. almost 20 years before James Watt steam engine. Polzunov not only created the world's first steam engine, but he also designed its distribution gear and for the first time accomplished automatic feeding of the boiler.

Until the fifties of the 19th century science considered heat as a special, weightless, indestructable and increatable substance, referred to as the caloric or phlogiston. The famous Russian scientist M. V. Lomonosov was the first to reject this theory. In 1774, in his thesis "On the Cause of Heat and Cold" he wrote that heat consists in the internal motion of matter proper and indicated that fire and heat consist in the rotation of motion of the particles which constitute all bodies. Thus, Lomonosov laid in his works the foundation of the mechanical theory of heat. However, Lomonosov was not understood by his contemporaries. Physicists continued for a long time to talk about phlogiston. Only in the middle of the 19th century, as a result of the work undertaken by a great number of scientists, the mechanical theory of heat was generally recognized and became the basis of thermodynamics and power engineering.

The discovery of the law of conservation and conversion of energy, as has been repeatedly pointed out by F. Engels, has essentially influenced the entire subsequent development not only of physics, but also of natural science as a whole. Engels considered this discovery to be one of the three great discoveries of the 19th century in natural science, which put dialectical-materialistic outlook on nature firm foundations.

M. V. Lomonosov was one of the first to propone the idea of the law of conservation of energy. In his work "On the Hardness and Liquidity of Bodies", in his letter to L. Euler of July 5, 1747 Lomonosov wrote that the origin of all changes occurring in nature consist in that whatever is removed from one body is added to another body in the same amount. So, when there is a decrease in matter in one place, matter increases in another place.... This general law is also true for the laws of motion: since a body, moving another one, loses as much force as it imparts to the other body.

This statement of Lomonosov does not yet contain quantitative relationships, nevertheless, it distinctly and fully conveys the essence of the law of conservation and conversion of energy. Not until a century later, due to the works of A. Lavoisier, A. Mayer, H. Helmholtz and others, has this law been generally recognized. In all fairness to the great foresight of Lomonosov, the law of conservation and conversion of energy is called after him.

In 1840, the Russian Academician, chemist G. Hess formulated the principle of conservation and conversion of energy as applied to chemical processes. Later on a great many Russian and Soviet scientists have widened

considerably the science of heat and have greatly contributed to the development of thermodynamics.

Applying the basic laws to processes involving conversion of heat into mechanical work and mechanical work into heat, engineering thermodynamics makes it possible to develop the theory of heat engines, investigate the processes occurring in them and permits determination of the efficiency of each type of engine separately.

1-3. International System of Units (SI)

In 1963, the USSR Standard, GOST 9867-61, prescribed that in the USSR preference should be given to the International Absolute System of Units (SI) in all branches of science and engineering.

The basic units in this system are: the unit of length—metre (m), the unit of mass—kilogramme (kg), the unit of time—second (s), the thermodynamic temperature—degree K (K). All other units are derivatives of the basic, or fundamental, units.

The unit of energy (as also of heat and work) is called the absolute joule (J), and is equal to the work performed by a force of 1 N over a path of 1 m when the direction of the force and of the displacement of the point of application coincide (1 J=1 N×1 m=1 kg m^2/s^2). The State Standard, GOST 8550-61, permits temporary use of another unit of power, the kilocalorie (1 kcal=4.1868×10^3 J).

The unit of power, the watt, (W), corresponds to the work equal to 1 J per 1 s (J/s).

Table 1-1 gives the relations between different units of energy.

TABLE 1-1

Measurement units	kJ	Kilocaloric	Kilogram·metre	Kilowatt·hour
Kilojoule (kJ)	1	0.239	102.0	0.000 278
Kilocalorie (kcal)	4.186 8	1	427	0.001 16
Kilogram·metre (kg m)	0.009 81	0.002 34	1	0.000 002 72
Kilowatt·hour (kW h)	3600	860	367 200	1
H.p.h (h.p.h)	2647.8	632.3	270 000	0.736

1-4. Basic Thermodynamic Parameters of State

The subject of engineering thermodynamics is mainly the study of processes of mutual conversion of heat and work in various heat engines, in which heat is converted into work with the aid of a so-called working medium (or fluid). In internal combustion engines, and also in gas-turbine plants, for instance, the processes considered involve a gas as a working

fluid. The working fluid in the processes developing in steam engines is steam that changes easily from the gaseous into the liquid state and, conversely, from the liquid state into the gaseous.

The physical state of a body is completely determined by certain quantities characterizing the given state. In thermodynamics these quantities are referred to as the *parameters of state.*

A whole number of quantities can serve as parameters e.q.: specific volume, pressure, temperature, internal energy, enthalpy, entropy, concentration, the isochoric-isothermal potential, etc.

However, in the absence of power fields (gravitational, electromagnetic, etc.) the state of a homogeneous body can be unambiguously determined by three parameters of state, which in engineering thermodynamics are the specific volume, absolute temperature and pressure. These three parameters of state, usually referred to as *basic*, are not independent quantities and, as will be shown below, are interrelated mathematically.

Specific volume. By the specific volume of a homogeneous substance is meant the volume occupied by a unit mass of the given substance. In engineering thermodynamics the specific volume is designated by v and measured in m^3/kg

$$v = V/m,$$

where V = volume in cubic metres (m^3) occupied by the mass m, in kg, of the substance.

The density of a body is defined as the mass per unit volume of substance and is measured in kg/m^3

$$\varrho = m/V.$$

The specific volume is the reciprocal of density, i.e.

$$v = 1/\varrho; \quad \varrho = 1/v; \quad v\varrho = 1.$$

Pressure. In terms of the molecular-kinetic theory pressure is the mean result of the impact of the molecules of a gas in continuous random motion against the walls of the confining vessel, and is equal to the normal resulting force acting on unit surface.

In SI system, the pressure is measured in newtons per square metre (N/m^2). Practical calculations permit the use of multiple and fraction pressure measurement units, such as the kilonewton per 1 m^2 (kN/m^2), meganewton per 1 m^2 (MN/m^2); pressure is often measured in bars (1 bar = $= 10^5$ N/m^2). It should be, however, borne in mind that in all thermodynamic formulae pressure must be substituted by units of newtons per square metre (N/m^2).

Pressure can also be measured by the column of liquid—mercury, water, alcohol, etc. that balances the pressure exerted by a gas. Figure 1-1 shows a vessel filled with a gas. The bent tube soldered to the wall of the vessel is filled with some liquid. The pressure inside the vessel, p_1, is greater than the atmospheric pressure, p_0. Acted upon by the difference in pressure

p_1-p_0 the liquid shall rise in the right side of the tube and balance the excess pressure in the vessel. We can write the equation

$$p_1F=p_0F+hF\varrho g,$$

whence

$$h=\frac{p_1-p_0}{\varrho g}$$

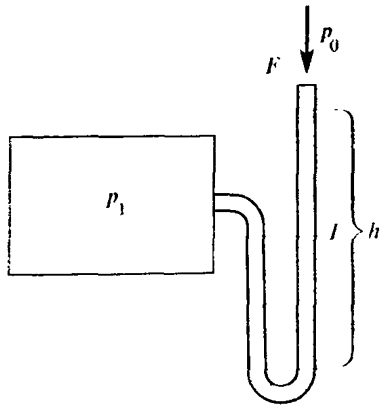


FIG. 1-1

The height of the column of liquid h is directly proportional to the difference between the pressure inside the vessel and the pressure of the surroundings and is inversely proportional to the density of the liquid used.

If the pressure difference is assumed equal to 1 bar, then the height of the mercury column h filling the tube is

$$h=\frac{10\times10^4}{13\,595.10\times9.81}=750.10 \text{ mm Hg},$$

where $\varrho=13\,595.10$ kg/m^3=density of mercury at 0 °C;
$g\cong9.81$ m/s^2=acceleration due to gravity, or free-fall acceleration (taken for the given point on the Earth surface).

When the tube is filled with water the height of the column

$$h=\frac{10\times10^4}{1000\times9.81}=10.20 \text{ m}.$$

Pressure is measured with barometers and manometers (pressure gauges) and rarefaction—with the aid of vacuummeters. Barometers are used to measure atmospheric pressure, and pressure gauges—to measure pressure exceeding atmospheric. The pressure above atmospheric is referred to as *excess pressure*.

Only absolute pressure is used as a thermodynamic parameter of state. By *absolute pressure* we mean the pressure read from absolute zero pressure or from absolute vacuum. While determining absolute pressure, two cases are distinguished:

(1) when the pressure in the vessel is higher than atmospheric and

(2) when the pressure is lower than atmospheric. In the first case the absolute pressure in the vessel is equal to the sum of the pressure readings of the barometer and pressure gauge (Fig. 1-2):

$$p_{abs}=p_{ex}+p_{atm}.$$

If the barometric pressure is not known then in expressing pressure in bars the absolute pressure $p_{abs}\approx p_{ex}+1$.

In the second case the absolute pressure inside the vessel is equal to the difference between the readings of the barometer and vacuummeter (Fig. 1-2)

$$p_{abs}=p_{atm}-p_{vac}.$$

Excess pressure and rarefaction (vacuum) are not parameters of state, since at the same absolute pressure these quantities may vary depending on atmospheric pressure.

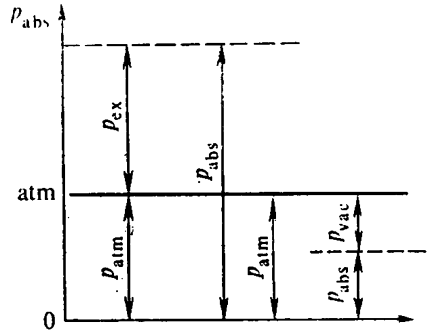


FIG. 1-2

Since the USSR State Standard, GOST 9867-61, permits simultaneous use of the old measurement units, the relation between different units of pressure is given for reference in conversion Table 1-2.

TABLE 1-2

	Physical atmosphere (atm)	Technical atmosphere (1 at = 1 kg/cm²)	Bar	Millimeters of mercury column (mm Hg)
1 atm	1	1.0332	1.0132	760.0
1 at	0.9678	1	0.9807	735.5
1 bar	0.9869	1.0197	1	750.1
10^3 mm Hg	1.3158	1.3595	1.3332	1000

Temperature, characterizing the degree of hotness of bodies, is a measure of the mean kinetic energy of translational motion of molecules, i.e. temperature characterizes the mean intensity of molecular motion, and the higher the mean velocity of molecular motion, the higher the temperature of a body. The concept of temperature cannot be applied to one or several molecules. If two bodies with different mean kinetic energies due to molecular motion, are brought into contact with each other, then the body with the larger mean kinetic energy (with a higher temperature) will transfer energy to the body with the smaller mean kinetic energy (with a lower temperature), and this process of heat transfer will continue till the mean

kinetic energies of the two bodies become equal, i.e. the temperatures of the two bodies become equal. Such a state of two bodies is referred to as *thermal equilibrium.*

With bodies in thermal equilibrium the kinetic theory of matter relates the mean kinetic energy of translational motion of molecules, $m\bar{w}^2/2$, with the absolute temperature of an ideal gas T by the following formula

$$m\bar{w}^2/2 = 3/2\, kT,$$

where m = mass of molecule;

$\bar{w}$ = root-mean square velocity of translational motion of molecules;

T = absolute temperature;

k = Boltzmann's constant, equal to 1.38×10^{-23} J/deg.

The absolute temperature is always positive. At the absolute zero temperature ($T=0$) the thermal motion of molecules terminates ($\bar{w}=0$). This limiting minimum temperature is the reference (fixed) point for taking readings of absolute temperature.

In engineering practice, various properties of bodies are used for measuring temperature: the expansion of bodies upon heating in liquid-filled thermometers; the change in volume at constant pressure or the change in pressure at constant volume in gas-filled thermometers; the change of the electrical resistance of a conductor upon heating in resistance thermometers; the change of the electromotive force in the circuit of a thermocouple upon heating or cooling of its junction. The measurement of high temperatures by means of optical pyrometers is based on the laws of emission from solids and on methods of comparing the incandescent filament with the material under investigation.

The USSR Standard, GOST 8550-61, specifies the use of two temperature scales: the thermodynamic temperature scale, based on the second law of thermodynamics, and the empirical temperature scale which is a practical realization of the thermodynamic temperature scale with the aid of fixed points and interpolation equations.

On either of these scales temperature can be measured both in degrees Kelvin (K) and in centigrade degrees (°C), depending on the reference point (zero position) of the scale assumed.

At the so-called triple point of water, i.e. at the point where the liquid, gas and solid phases are in equilibrium the temperature in degrees Kelvin is 273.16 K (exactly) and 0.01 °C in degrees Celsius (centigrade).

Hence, temperatures expressed in degrees Kelvin and degrees Celsius are interrelated as follows

$$T\,\text{K} = 273.15 + t\ ^\circ\text{C}.$$

The absolute temperature, measured in degrees Kelvin, is a parameter of state. The degree on the absolute scale is equal numerically to the degree of centigrade, or Celsius, scale, so that $dT = dt$.

1-5. Thermodynamic System

Any natural phenomenon involves the action of a great number of various bodies that are interrelated in one way or another. When the method of thermodynamics is used to investigate any phenomenon, a group of bodies or a single body, or even its individual component parts are singled out as the object of investigation. The object of the study is called a *thermodynamic system* and all the other bodies located outside its boundaries are referred to as the *surroundings*. A thermodynamic system is defined as the totality of macroscopic bodies exchanging energy both with one another and with the external medium or surroundings.

The simplest example of a thermodynamic system (body) is a gas confined within a cylinder with a piston. Considered as parts of the surroundings must be the cylinder and piston, the air surrounding them, the walls of the room where the cylinder and piston are placed, etc. If the thermodynamic system does not interact in any way with the surroundings, it is referred to as a *closed*, or isolated *system.*

A system surrounded by a so-called adiabatic envelope, precluding heat transfer to or from the surroundings, is called a *heat-insulated*, or adiabatic, *system.* An example of an adiabatic system is the working fluid held in a vessel whose walls are covered with an ideal heat insulating material thereby ruling out heat exchange between the working fluid and the surroundings.

A system whose composition and physical properties are similar in all its parts is known as a physically *homogeneous system.* Examples of homogeneous thermodynamic systems (both in respect to composition and physical properties) in which there are no interfaces is called a *homogeneous* one (for instance, ice, water and gases).

A system consisting of several macroscopic parts with different physical properties, separated from one another by visible interfaces is called a *heterogeneous* system [for instance, ice and water, water and steam etc.].

The homogeneous parts of a system separated from the other parts of the system by visible interfaces are referred to as *phases.* Depending on the number of phases, heterogeneous systems are said to be *two-phase* and *three-phase* systems (with gaseous, liquid and solid states). By the *component* of a thermodynamic system is meant any chemically homogeneous system.

1-6. Thermodynamic Process

The basic thermodynamic parameters of state p, v and T of a homogeneous body depend on one another and are interrelated by a definite mathematical equation of the kind

$$F(p, v, T)=0,$$

which, in thermodynamics, is called the *equation of state.* If the equation of state is known, then in order to determine the state of simplest sys-

tems—homogeneous and constant in time, mass and composition (consisting of one phase and not varying chemically)—it is sufficient to know two independent variables out of the three

$$p=f_1(v, T); \quad v=f_2(p, T); \quad T=f_3(v, p).$$

If the conditions of the external medium surrounding the thermodynamic system change, the state of the system shall also change. The totality of the changes of state that the thermodynamic system undergoes while passing from one equilibrium state into another is referred to as a *thermodynamic process.*

A body is said to be in *equilibrium* state, if its temperature, pressure, specific volume and all other physical properties are the same over the entire volume of the system.

A system may undergo an equilibrium and non-equilibrium change of state. If a process passes in its development through a succession of equilibrium states, it is called an *equilibrium* process.

Thermodynamics considers primarily equilibrium states and the equilibrium processes a system undergoes when changing its state. Only equilibrium states can be described quantitatively with the aid of an equation of state. The simplest equations of state are the Clapeyron, Clapeyron-Mendeleyev, van-der-Waals and other equations that shall be considered in detail in the following chapters.

An equilibrium process can be realized through an infinitely slow change of external conditions, or when the variations of the parameters characterizing the state of a system are infinitely small compared with the magnitudes of parameters. Consequently, real processes, being of a non-equilibrium nature, can approach equilibrium processes, never coinciding exactly with them.

The non-equilibrium nature of real processes is determined primarily by the fact that, under the effect of external conditions, they proceed with finite speeds (velocities) and the working fluid has no time to pass into the equilibrium state. For instance, when a gas expands rapidly in a cylinder underneath a piston or if it is compressed quickly, the temperature and pressure will not be the same at different points over the volume of the working fluid, i.e. a non-equilibrium state shall set in and the process itself will be a *non-equilibrium* one.

From mathematical point of view, in p, v and T three-axis system of coordinates the equation of state $F(p, v, T)=0$ expresses some surface which is called the *thermodynamic surface.*

The equilibrium processes which a system undergoes when it changes its state can be represented graphically. In fact, any arbitrary equilibrium state shall be represented on the thermodynamic surface by a point, and when the system undergoes a continuous succession of equilibrium states the set of points shall be represented on the surface by a curve which is the graphical representation of an equilibrium process. It is rather incovenient to use three-axis system of coordinates, therefore processes are depicted

not by curves, but by their projections on a plane in rectangular coordinates.

If the thermodynamic surface is cut with planes parallel to the coordinate axes, we obtain the following curves on the surface: cutting with a plane $v=\text{const}$ produces a line characterizing the process of a change in pressure against temperature in p-T coordinates; the process described by this line occurs at a constant volume and is referred to as an *isochoric* (constant-volume) process; cutting with a plane $p=\text{const}$ yields a line characterizing the change in specific volume against temperature in v-T coordinates; the process described by this line occurs at a constant pressure and is called the *isobaric* (constant-pressure) process; cutting the thermodynamic surface with a plane $T=\text{const}$ produces a line characterizing the change in pressure depending on specific volume at a constant temperature in p-v coordinates. The process described by this line is said to be an *isothermal* one.

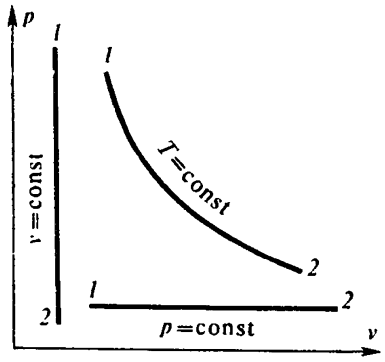


FIG. 1-3

In engineering thermodynamics equilibrium thermodynamic processes are usually investigated with the aid of the p-v system of coordinates in which plotted on the x-axis is the specific volume, and on the y-axis—pressure.

In the p-v coordinates vertical lines depict processes occurring at a constant volume, i.e. isochoric ones, and the horizontal lines represent processes realized at a constant pressure—isobaric processes; processes occurring at constant temperature are represented in the p-v coordinates by a hyperbola-like curve (gaseous state), and are called isothermal (Fig. 1-3).

In studying thermodynamic processes, of special importance are the so-called *closed* or *cyclic* processes in the course of which, having passed through a succession of states, a system comes back to its initial state. A closed process is also referred to as a *cycle*.

In any thermodynamic process the change of a parameter of state is independent of the nature of process and is completely determined by the initial and final states. Therefore, any parameter of state can also be said to be a function of state. A number of other functions of state, such as internal energy, enthalpy and entropy shall be treated below.

It should be noted that parameters (functions of state) may or may not depend on the mass of the system. The parameters of state that are independent of the mass of a system are referred to as *intensive parameters* (pressure, temperature, etc.). The parameters of state whose magnitudes are proportional to the mass of a system are called *additive* or *extensive parameters* (volume, energy, entropy, etc.).

1-7. Heat and Work

Marxist dialectics teaches that motion is an inherent property of matter and is indestructible as matter itself. The motion of matter manifests itself in various forms which may transform one into another. The measure of motion of matter is energy.

It has been shown experimentally that the bodies taking part in a thermodynamic process exchange energy with one another as the process occurs, with the result that the energy of some bodies increases, and of others—diminishes.

In the course of a process energy can be transferred from one body to another in two ways.

The first method of energy transfer is realized in bodies at different temperature in direct contact through an exchange of kinetic energy between the molecules of the contacting bodies, or by means of radiant transfer of internal energy of emitting bodies by electromagnetic waves. Energy is then transferred from a body at a higher temperature to a body at a lower temperature, i.e. from a body possessing a larger mean kinetic energy of molecules to a body with a smaller mean kinetic energy of molecules. The amount of energy transferred by the first method from one body to another is called the *quantity of heat*, and the method involved—transfer of energy in the form of heat. The amount of energy received by a body in the form of heat shall be referred to below as *added* heat, and the amount of energy given away by a body in the form of heat—as *rejected* (removed) heat.

Just as any other form of energy, heat is measured in joules or kilojoules. An arbitrary quantity of heat is denoted by Q, and the specific heat corresponding to 1 kg—by q. Added heat is assumed to be *positive*, and rejected heat—*negative*.

The second method of energy transfer is associated with the presence of fields of force or with external pressure. For energy to be transferred by this method a body must either move in a field of force or change its volume when acted upon by external pressure. In other words, energy in this case is transferred under conditions of movements in space of the entire body or its parts.

This method of energy transfer is called the *method of energy transfer in the form of work*, and the amount of energy transferred in the course of the process is referred to as *work*.

The amount of energy transferred to a body in the form of work shall be referred to below as the work *done* on the body, and the energy transferred from the body—as the work *expended*, or spent, by the body. Work is also measured in joules or kilojoules. The work expended by a body is considered to be *positive*, and the work done on a body—*negative*. An arbitrary amount of energy transferred in the form of work is denoted by L, and the specific work—by l.

In the general case energy can be transferred in the forms of heat and work simultaneously. It should be emphasized that in various thermodynamic

processes the amounts of heat and work involved shall differ depending on the conditions under which processes occur.

It follows that heat and work characterize qualitatively and quantitatively two different forms of transmission of motion from one material bodies to others.

Work is the macrophysical form of energy transfer and heat is the totality of microphysical processes, inasmuch as energy is transferred then on a molecular scale without apparent motion of the bodies involved. For instance, a change in molecular velocity and energy transfer due to molecular collisions, emission of light quanta, profound changes of the very structure of molecules and atoms, etc. All these energy transformations, that cannot be observed in ordinary conditions, manifest themselves and are perceived by us in the form of heat. The amounts of work and heat are the measures of the energy transferred to bodies in the forms of work and heat.

The quantity of heat transferred to a body and the work done by the body depend on the conditions under which the body passes from the initial into the final state, i.e. on the nature of the process. The concept of "heat and work" originates only in connection with thermodynamic process and, if there is no process, there is no heat and work. That is why it cannot be said that there is a store of heat or work in a body.

From this it follows that neither elementary work dL, nor elementary heat dQ are complete differentials of parameters of state and they cannot be referred to as increments of the quantities of heat and work. The quantities dQ and dL only represent infinitely small amounts of heat and work participating in an elementary process. That is why for a finite process we cannot write that

$$\int_1^2 dQ = Q_2 - Q_1 \quad \text{and} \quad \int_1^2 dL = L_2 - L_1.$$

The two integrals can be taken only when special data between the states 1-2 are assumed, i.e. the conditions under which the process takes place. Therefore, the integration can only be designated as follows

$$\int_1^2 dQ = Q_{1\text{-}2}; \quad \int_1^2 dL = L_{1\text{-}2}.$$

Thus, when dealing with thermodynamic processes involving a change of state heat and work are the only two possible ways of energy transfer from one body to another.

1-8. Thermodynamic Equilibrium

If the state of all bodies composing a thermodynamic system does not change for a long period of time, the system is said to be in *thermodynamic equilibrium.*

If in a thermodynamic system, having no heat-insulated and absolutely rigid partitions, bodies or parts of bodies are not in the same state, then after the expiry of some time (sooner or later) the system shall acquire (come into) a state of stable thermodynamic equilibrium.

In the state of thermodynamic equilibrium there is no heat transfer from some parts of the system to others, not do individual parts of the system move with respect to one another, i.e. the system is in thermal and mechanical equilibrium.

In thermodynamic equilibrium the pressure and temperature of all bodies composing the system shall be equal to the temperature and pressure of the surroundings. A change in the external conditions of the surroundings shall bring about a change in the state of the system, and this change can be observed until the pressures and temperatures of the surroundings and system become equal, i.e. until stable equilibrium sets in.

Without an external disturbance (spontaneously) a system cannot pass out of the state of equilibrium.

Typical Questions and Examples to Chapter One

1. What is the essence of the first and second laws of thermodynamics?
2. What constitutes the limitation of the second law of thermodynamics?
3. What are the main subjects treated by engineering thermodynamics?
4. The international system of units (SI) and its basic units.
5. What quantities are referred to as thermodynamic parameters of state?
6. Which of the thermodynamic parameters of state are classified as basic or fundamental?
7. Write down the dimension of basic parameters of state.
8. Definition of specific volume and density of a gas.
9. How is the height of a column of liquid in measuring pressure determined?
10. What is the difference between absolute and manometer (gauge, or excess) pressure?
11. Name the temperature scales used in the USSR.
12. What is meant by absolute temperature?
13. What is referred to as the equation of state?
14. What is the definition of the state of equilibrium?
15. What is meant by thermodynamic processes and how do they proceed?
16. What is a thermodynamic system?
17. Define the homogeneous and heterogeneous systems.
18. What is the definition of a cyclic process (cycle)?
19. Which are the forms of energy transfer from one bodies to others?
20. What is meant by thermodynamic equilibrium?
21. The conditions for the existence of a complete differential.
22. Characteristics of identical equations.

Example 1-1. Determine the specific volume and density of air, if 77.58 kg of it occupies a volume of 60 m^3.

Answer. $v=0.774$ m^3/kg; $\varrho=1.293$ kg/m^3.

Example 1-2. Determine the absolute pressure of a gas confined in a vessel, if the reading of a mercury-filled glass manometer is equal to 375 mm Hg, and a barometer shows the pressure of 750 mm Hg. The two instruments are at a temperature of 0 °C. Express the pressure in bars:

$p_{abs}=p_{ex}+p_{atm}=1.5$ bar

Example 1-3. A mercury-column vacuummeter, connected to a condenser indicates a pressure of 512.5 mm Hg at a temperature of 0 °C. Atmospheric pressure as indicated by a mercury barometer at the same temperature is 729 mm Hg. Determine the absolute pressure in the condenser, expressing the pressure in bars. The pressure of 512.5 mm Hg corresponds to a pressure of 75 000 N/m^2, and the pressure of 729 mm Hg is equal to 97 400 N/m^2.

$p_{abs}=p_{atm}-p_{vac}=97\,400-75\,000=22\,400$ $N/m^2=0.224$ bar.

CHAPTER TWO

EQUATION OF STATE FOR IDEAL (PERFECT) GASES

2-1. Basic Laws Governing the Behaviour of Ideal Gases

The *ideal*, or *perfect* gases, are gases that fully obey Boyle's and Gay-Lussac's laws. Ideal gases are characterized by the absence of forces due to mutual attraction and repulsion between the molecules, and the volume occupied by the molecules is infinitely small compared with that of the gas.

At high temperatures and low pressures all real gases can be treated as an ideal gas and their properties practically do not differ from those of an ideal gas. The state of an ideal gas is the limiting state for a real gas, when pressure tends to zero ($p \to 0$).

Introduction of the concept of an ideal, or perfect, gas made it possible to relate mathematically the quantities characterizing the state of a body and to use the ideal gas laws to create the theory of thermodynamic processes.

Boyle's law relates the specific volume and absolute pressure of an ideal gas undergoing a process at a constant temperature. This law was discovered experimentally in 1664 by the English physicist R. Boyle, and independently by the French chemist E. Mariotte in 1676.

Boyle's law states that *at constant temperature the volume occupied by an ideal gas varies inversely with its pressure:*

$$v_1/v_2 = p_2/p_1 \tag{2-1}$$

Or, at constant temperature the product of the specific volume of a gas and its pressure is constant

$$p_1v_1 = p_2v_2, \quad pv = \text{const.}$$

In p-v coordinates Boyle's law is represented by an equilateral hyperbola as illustrated in Fig. 1-3. This curve has been given the name of an *isotherm* and the process occurring at a constant temperature is known as an isothermal process.

Gay-Lussac's law relates specific volume and absolute temperature at constant pressure. This law was discovered experimentally by the French physicist Joseph Louis Gay-Lussac in 1802.

Gay-Lussac's law states that *at constant pressure the volumes of the same quantities of an ideal gas change directly with absolute temperatures*

$$v_1/v_2 = T_1/T_2. \tag{2-2}$$

In p-v coordinates Gay-Lussac's law is represented by a line running parallel to the x-axis (Fig. 1-3). This line is called an *isobar*, and the process itself is referred to as an *isobaric* or constant-pressure thermodynamic process.

2-2. Equation of State of Ideal Gases

As was mentioned above, the main parameters of state (absolute pressure, specific volume and absolute temperature) of a homogeneous body depend on one another and are interrelated by the mathematical equation of the form

$$F(p, v, T)=0,$$

which is referred to as the *equation of state.*

This equation holds both for real and ideal gases. However, because of serious inherent difficulties involved, it has been impossible so far to derive a universal equation for real gases which would embrace all the changes in their states. The simplest equation of state can be obtained for an ideal gas.

It follows from the molecular-kinetic theory of heat that absolute pressure of a gas is numerically equal to 2/3 of the mean kinetic energy of the translational motion of molecules confined in unit volume

$$p=\frac{2}{3}\frac{n}{v}\frac{m\overline{w}^2}{2}, \tag{2-3}$$

where n = number of molecules in volume v;
v = volume of 1 kg of gas;
m = molecular mass;
$\overline{w}$ = root-mean square velocity of translational molecular motion;
$\frac{m\overline{w}^2}{2}$ = mean kinetic molecular energy.

The molecular-kinetic theory of gases establishes a direct proportionality between the mean kinetic energy of molecules and absolute temperature

$$\frac{m\overline{w}^2}{2}=BT,$$

where T = absolute temperature;
B = factor of proportionality.

With the help of this equality, equation (2-3) can be presented in the following form

$$pv=\frac{2}{3}nBT. \tag{2-4}$$

Relating equation (2-4) to the two parameters of state, we obtain for each of them

$$p_1v_1=\frac{2}{3}nBT_1 \quad \text{or} \quad p_2v_2=\frac{2}{3}nBT_2.$$

Dividing termwise these equations, we arrive to the following relationship

$$p_1v_1/T_1=p_2v_2/T_2. \tag{2-5}$$

The relation between parameters (2-5) can also be found by considering together Boyle's and Gay-Lussac's laws, that is why this relationship is called the combined Boyle-Gay-Lussac law.

Relationship (2-5) shows that the product of the specific volume of an ideal gas and absolute pressure, divided by absolute temperature is constant for any equilibrium state:

$$pv/T=\text{const}. \tag{2-6}$$

The constant quantity, corresponding to 1 kg of gas, is denoted by the letter R and is called the *gas constant*

$$pv/T=R, \quad \text{or} \quad pv=RT. \tag{2-7}$$

Equation (2-7) is called the *thermal equation of state* of ideal gases or the *characteristic equation.* It relates singularly the parameters p, v and T. The equation of state for ideal gases was derived by the French physicist B. Clapeyron in 1834 and is therefore named after him.

For an arbitrary quantity of gas with mass m kg, the equation of state acquires the following appearance:

$$pV=mRT,$$

where p = absolute pressure of the gas, N/m^2;
V = volume of arbitrary quantity of gas, m^3;
m = mass of gas, kg;
T = absolute temperature of the gas, K.

The gas constant R is a physical constant which has a definite value for each gas, depending on its nature and independent of its state.

Let us elucidate the physical meaning of the gas constant, writing Clapeyron's equation for the first state

$$pV_1=mRT_1;$$

for the second state at the same pressure

$$pV_2=mRT_2.$$

Subtracting the first equation from the second, we obtain

$$p(V_2-V_1)=mR(T_2-T_1),$$

whence

$$R=\frac{p(V_2-V_1)}{m(T_2-T_1)}.$$

The numerator in the right-hand side of the above equation represents the work done by the gas in the process at constant pressure. If the tempera-

ture difference (T_2-T_1) is equal to 1°, and the mass of gas is 1 kg, then the gas constant represents the work, measured in joules, done by 1 kg of the gas in the process at constant pressure with the temperature varying by 1°.

The dimension of the gas constant is as follows

$$R=\frac{p(V_2-V_1)}{m(T_2-T_1)}=\frac{\text{N/m}^2\cdot\text{m}^3}{\text{kg}\cdot\text{deg}}=\frac{\text{N}\cdot\text{m}}{\text{kg}\cdot\text{deg}}=\frac{\text{J}}{\text{kg}\cdot\text{deg}}.$$

When presented in this form Clapeyron's equation is true only for ideal gases. However, this equation can be applied with sufficient practical accuracy to real gases at low pressure and high temperature.

2-3. Universal Equation of State for Ideal Gases

Clapeyron's equation can be made universal by relating the gas constant not to 1 kg of gas, but to 1 kmole.

The Italian scientist A. Avogadro proved in 1811 that equal volumes of ideal gases at the same temperature and pressure contain equal numbers of molecules. It follows from Avogadro's law that the densities of gases at equal temperatures and pressures are directly proportional to their molecular masses

$$\frac{\varrho_1}{\varrho_2}=\frac{\mu_1}{\mu_2}, \qquad \text{(a)}$$

where μ_1, μ_2= molecular masses of gases.

By the *molecular mass* of a gas is meant the *numerical value of the ratio of the mass of a molecule of a given substance to 1/12 mass of the atom of the carbon isotope* ^{12}C.

The quantity of substance containing as many molecules (atoms of particles) as the number of atoms contained in the nuclide of carbon ^{12}C with a mass of 12 kg (exactly) is called a *kilogram-molecule* or *kilomole* of gas (kmole).

The ratio of densities of gases can be replaced in Eq. (a) with the inverse ratio of specific volumes. Then,

$$v_2/v_1=\mu_1/\mu_2 \quad \text{whence} \quad v_1\mu_1=v_2\mu_2.$$

This relation shows that under the same physical conditions the product of the specific volume of a gas and its molecular mass is constant and independent of the nature of the gas

$$v\mu=\text{const.} \qquad \text{(2-8)}$$

The product $v\mu$ is the volume of 1 kmole of ideal gas, and Eq. (2.8) shows that the volumes of kilomoles of all gases at the same temperatures and pressures are equal.

Let us write the equation of state for 1 kmole of gas

$$pV_\mu=\mu RT, \qquad \text{(2-9)}$$

whence

$$\mu R=\frac{pV_\mu}{T}.$$

The product μR is called the *universal gas constant.*

The universal gas constant is the work performed by 1 kmole of ideal gas in a process occurring at constant pressure and for a 1° change in temperature.

Under the so-called standard physical conditions (at pressure of 101 325 N/m² and temperature of 273.15 K) the volume of 1 kmole of gas is equal to 22.4143 m³/kmole, and the universal gas constant turns out to be equal to

$$\mu R=\frac{101\,325\times 22.4143}{273.15}=8314.20 \text{ J/kmole·deg}=8.3142 \text{ kJ/kmole·deg}.$$

The universal equation of state, related to 1 kmole of gas takes the following appearance

$$\rho V_\mu=8314.20T. \qquad (2\text{-}10)$$

Equation (2-10) is called the *Clapeyron-Mendeleyev equation of state,* since it was Mendeleyev who first suggested it in 1874. Clapeyron-Mendeleyev's equation is the most general one for ideal gases, for it relates three ideal gas laws (Gay-Lussac's, Boyle's and Avogadro's), and includes the universal gas constant that is independent of the nature of gas.

Knowing the universal gas constant μR, we can calculate the already known quantity R

$$R=8314.2/\mu \text{ J/kg·deg}.$$

The physical constants of some gases are given in Table 2-1.

TABLE 2-1

Gas	Chemical formula	Mass of 1 kmole, kg/kmole	Gas constant R, J/kg·deg	Gas density in standard physical conditions, kg/m³
Oxygen	O_2	32	259.8	1.429
Hydrogen	H_2	2.016	4124.3	0.090
Nitrogen	N_2	28.02	296.8	1.250
Carbon monoxide	CO	28	296.8	1.250
Air	—	28.96	287.0	1.293
Carbon dioxide	CO_2	44	189.9	1.977
Water vapour	H_2O	18.016	461.6	0.804
Helium	He	4.003	2077.2	0.178
Argon	Ar	39.944	208.2	1.784
Ammonia	NH_3	17.031	488.2	0.771

Equation (2-7) can be used to establish some important relations between thermodynamic parameters of state. For an ideal gas the partial derivatives of the main parameters of state acquire the following appearance: differentiating the equation $pv=RT$, we obtain $pdv+vdp=RdT$; at $p=\text{const}$ $(\partial v/\partial T)_p=R/p$; at $v=\text{const}$ $(\partial p/\partial T)_v=R/v$; at $T=\text{const}$ $(\partial v/\partial p)_T=-RT/p^2$ and $(\partial p/\partial v)_T=-RTv^2$.

The product of the partial derivatives for an ideal gas turns into -1

$$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial T}{\partial p}\right)_v=-\frac{R}{p}\,\frac{v}{R}\,\frac{RT}{v^2}=-1.$$

Typical Questions and Examples to Chapter Two

1. For what purpose is the concept of an ideal gas introduced into engineering thermodynamics?
2. What are the definitions and equations for the Boyle-Gay-Lussac law?
3. What is meant by the molecular mass of a gas?
4. The characteristic equation of state of an ideal gas.
5. What laws were used as a basis in deriving Clapeyron's equation of state?
6. The Clapeyron equation for an arbitrary quantity of gas.
7. The dimensions of all the quantities in Clapeyron's equation of state.
8. What are the dimensions of the gas constant and what is its physical meaning?
9. What is referred to as a kilomole of a gas?
10. Avogadro's law, its definition and conclusions.
11. What laws serve as basis in deriving Mendeleyev's equation?
12. Give the definition of the universal gas constant and its dimensions.

Example 2-1. Determine the density and specific volume of carbon monoxide CO at a pressure of 1 bar and a temperature of 300 K.

The specific volume can be found from Clapeyron's equation

$$v=\frac{RT}{p}=\frac{297.4\times 300}{1\times 10^5}=0.89\ \text{m}^3/\text{kg}.$$

The density of carbon monoxide

$$\varrho=1/v=1/0.89=1.125\ \text{kg/m}^3$$

Example 2-2. To determine the heat of fuel combustion in a calorimeter bomb, we use oxygen taken from a cylinder, or bottle, of 0.006 m^3 capacity at an absolute pressure $p=120$ bar and a temperature $T=300$ K. Determine the number of oxygen charges that can be made if the volume of the calorimeter bomb is 0.0004 m^3 and the absolute pressure of the oxygen in the bomb is 22 bar at a temperature $T=300$ K.

Clapeyron's equation is used to determine the mass of oxygen in the cylinder

$$m_1=\frac{pV}{RT}=\frac{120\times10^5\times0.006}{259.8\times300}=0.925 \text{ kg.}$$

The unconsumed mass of oxygen left in the cylinder is

$$m_2=\frac{pV}{RT}=\frac{22\times10^5\times0.006}{250.8\times300}=0.169 \text{ kg.}$$

The amount of oxygen consumed is equal to

$$m_1-m_2=0.925-0.169=0.756 \text{ kg}$$

The mass of oxygen used for charging the calorimeter bomb is

$$m_3=\frac{pV}{RT}=\frac{22\times10^5\times0.0004}{259.82\times300}=0.01125 \text{ kg.}$$

The number of oxygen charges that can be made is

$$(m_1-m_2)/m_3=0.756/0.01125=67.$$

Example 2-3. Determine the payload that can be lifted with the aid of an aerostat (balloon) of a volume of 1000 m^3 at a temperature $T=300$ K and a pressure $p=1$ bar, if the balloon is filled with hydrogen.

The mass of air that is displaced by the balloon is

$$\frac{pV}{RT}=\frac{1\times10^5\times1000}{287\times300}=1163 \text{ kg.}$$

The mass of hydrogen filling the balloon is

$$m_2=\frac{pV}{RT}=\frac{1\times10^5\times1000}{4124\times300}=81 \text{ kg.}$$

The buoyancy (lift force) of the balloon is

$$1163-81=1082 \text{ kg.}$$

Example 2-4. Determine the mass of oxygen in a cylinder of 200 *l* capacity at a pressure $p=120$ bar and a temperature $T=17$ °C.

Answer. $m=16$ kg.

CHAPTER THREE

MIXTURES OF IDEAL GASES

3-1. Basic Properties of Mixtures of Gases

Practical engineering often has to deal with gaseous substances, whose properties make them close to ideal gases, representing the mechanical mixture of individual gases, for instance, blast-furnace gas, lighting gas, the flue gas from boiler units, from internal combustion engines, reaction engines and from other heat installations. Atmospheric air is also a mixture of gases composed of nitrogen, oxygen, carbon dioxide, water vapour and monoatomic gases. Therefore, to solve practical problems, we must be able to determine the basic properties of gas mixture, such as the gas constant, mean molecular mass, partial pressures, etc.

By a *gas mixture* is meant a mixture of gases not reacting chemically with one another. Independent of the other gas components of a mixture, each gas fully preserves its properties and behaves as though it alone occupies the entire volume of the mixture. The molecules of the gas exert pressure on the walls of the confining vessel, which is called the *partial* pressure. It will be assumed below that each individual gas component of the mixture obeys Clapeyron's equation of state, i.e. is an ideal gas.

A mixture of ideal gases obeys Dalton's law, which states that the *total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gas components of the mixture*

$$p=p_1+p_2+\ldots+p_n=\sum_1^n p_i, \tag{3-1}$$

where $p_1, p_2, \ldots, p_n$ are partial pressures.

Partial pressure is defined as the pressure which each individual component of a gas mixture would exert if it alone occupied the volume of the mixture at the same temperature.

The properties of a gas mixture can be calculated from Clapeyron's equation

$$pV=mRT,$$

where all quantities pertain to the mixture of gases.

Thus, in calculating the gas mixture, the objective is to determine the mean molecular mass on the basis of the given composition of the mixture, or the gas constant of the gas mixture, then all other parameters of the mixture can be determined from the equation of state.

It is often also necessary to determine the partial pressures of the components of a mixture of gases.

In treating gas mixtures below, all quantities without subscripts shall pertain to gas mixtures and quantities with subscripts—to individual gases.

Methods of pre-assigning mixtures of gases. A gas mixture can be given in mass, volume and molar fractions.

The mass fraction of each component of a mixture is defined as the ratio of the mass of a given component to the mass of the entire mixture

$$g_1=m_1/m; \quad g_2=m_2/m; \quad \ldots; \quad g_n=m_n/m,$$

where $g_1, g_2, \ldots, g_n$ = mass fractions;
$m_1, m_2, \ldots, m_n$ = mass of each gas component;
m = mass of entire mixture of gases.

The sum of the mass fractions is equal to unity

$$g_1+g_2+\ldots+g_n=\sum_1^n g_i=1.$$

The sum of the masses of all gases is equal to the mass of the mixture of gases

$$m_1+m_2+\ldots+m_n=\sum_1^n m_i=m.$$

The volume fraction is defined as the ratio of the partial (reduced) volume of each gas to the total volume of the mixture

$$r_1=V_1/V; \quad r_2=V_2/V; \quad \ldots; \quad r_n=V_n/V,$$

where $r_1, r_2, \ldots, r_n$ = volume fractions;
$V_1, V_2, \ldots, V_n$ = partial volumes of each gas;
V = volume of the entire mixture of gases.

By the *partial volume* of a gas is meant the volume that this gas would occupy if its temperature and pressure were equal to the temperature and pressure of the mixture of gases.

The partial volume of each gas can be determined from Boyle's law. At constant temperature we have

$$V_1=p_1V/p; \quad V_2=p_2V/p; \quad \ldots; \quad V_n=p_nV/p.$$

Adding these equations, we obtain

$$V_1+V_2+\ldots+V_n=\sum_1^n V_i=V.$$

The sum of the partial volumes of the gases composing a mixture is equal to the volume of the gas mixture.

The sum of volume fractions is equal to unity

$$r_1+r_2+\ldots+r_n=\sum_1^n r_i=1.$$

Giving a mixture of gases in molar fractions is equivalent to specifying the mixture in volume fractions.

In fact, if a molar fraction is defined as the ratio of the number of kilomoles of each gas, M_i, to the number of kilomoles contained in the gas mixture, then, allowing for

$$\mu_i=m_i/M_i \quad \text{and} \quad \mu=m/M,$$

we can write

$$\frac{M_i}{M}=\frac{m_i}{m}\frac{\mu}{\mu_i}=\frac{\varrho_i V_i \mu}{\varrho V \mu_i}.$$

It follows from Avogadro's law that at the same pressures and temperatures

$$\varrho_i/\varrho=\mu_i/\mu.$$

Then, finally,

$$M_i/M=V_i/V=r_i.$$

The relation between mass and volume fractions. On the basis of Avogadro's law and Clapeyron-Mendeleyev's equation, the specific volumes, densities, molar masses and the gas constants of any gas are related to those of the entire gas mixture as follows

$$\varrho_i/\varrho=v/v_i=\mu_i/\mu=R/R_i, \tag{3-2}$$

where ϱ_i = density of each gas component;
ϱ = density of the gas mixture;
μ_i = molecular mass of each gas;
μ = molecular mass of the gas mixture.

It also follows that

$$g_i=m_i/m=\varrho_i V_i/\varrho V=(\varrho_i/\varrho)r_i.$$

The last two relationships permit working out of equations interrelating the mass and volume fractions

$$g_i=(v/v_i)r_i=(\mu_i/\mu)r_i=(R/R_i)r_i; \tag{3-2'}$$

$$r_i=(\varrho/\varrho_i)g_i=(v_i/v)g_i=(R_i/R)g_i=(\mu/\mu_i)g_i \tag{3-2''}$$

3-2. Gas Constant of a Gas Mixture

A mixture of gases obeys the equation of state

$$\varrho V=mRT \quad \text{and} \quad R=\frac{pV}{mT}.$$

It follows from Eq. (3-2″) that

$$r_i = g_i R_i / R \quad \text{and} \quad \sum r_i = \sum g_i R_i / R = 1,$$

whence

$$R = \sum g_i R_i = g_1 R_1 + g_2 R_2 + \ldots + g_n R_n . \tag{3-3}$$

The gas constant for a gas mixture is equal to the sum of the products of the mass fractions of each gas by its gas constant.

Another equation for determining the gas constant of mixture is of the following form

$$R = \sum g_i R_i = 8\,314.2\,(g_1/\mu_1 + g_2/\mu_2 + \ldots + g_n/\mu_n). \tag{3-4}$$

The gas constant of a gas mixture can be determined by the known mean molecular mass of the mixture

$$R = 8314.2/\mu. \tag{3-5}$$

Hence, the gas constant of a gas mixture is determined from the equation containing the mean molecular mass, and the gas constant of each individual gas is determined from the same equation but in this case the mean molecular mass is substituted with the real molecular mass of each gas component of the mixture.

If the volume composition of a mixture is given, then it follows from Eq. (3-2′) that

$$g_i = (R/R_i) r_i \quad \text{and} \quad \sum g_i = R \sum (r_i/R_i) = 1.$$

Then

$$R = \frac{1}{\sum (r_i/R_i)} = \frac{1}{r_1/R_1 + r_2/R_2 + \ldots + r_n/R_n} . \tag{3-6}$$

3-3. Mean Molecular Mass of a Gas Mixture

The mean molecular mass of a gas mixture is an arbitrary quantity which is related to such a homogeneous gas whose number of molecules and the total mass are equal to the number of molecules and the mass of the mixture of gases.

If the gas constant of a gas mixture is known, then

$$\mu = 8314.2/R \tag{3-7}$$

and

$$\mu = 8314.2/(g_1 R_1 + g_2 R_2 + \ldots + g_n R_n).$$

Substituting the gas constants R_1, R_2, ..., R_n with their values taken from Clapeyron's equation, we obtain the expression for the mean molecular mass, if the mixture is given in mass fractions

$$\mu = \frac{1}{g_1/\mu_1 + g_2/\mu_2 + \ldots + g_n/\mu_n} . \tag{3-8}$$

If the composition of the mixture is given in volume fractions then, as it follows from Eq. (3-6),

$$R=\frac{1}{\sum(r_i/R_i)}=\frac{8314.2}{\sum(r_i\mu_i)}.$$

Inasmuch as

$R=8314.2/\mu$,

then

$$\mu=\sum r_i\mu_i=r_1\mu_1+r_2\mu_2+\ldots+r_n\mu_n. \tag{3-9}$$

The mean molecular mass of a mixture of gases is equal to the sum of the products of the volume fractions by the molecular masses of individual gas components of the mixture.

3-4. Partial Pressure

The partial pressure of a gas can be determined in terms of the mass fractions from Clapeyron's equation, if the main parameters of the gas involved are known

$$p_i=\frac{m_iR_iT}{V}=p\frac{m_iR_i}{mR}=pg_i\frac{R_i}{R}=pg_i\frac{\mu}{\mu_i}. \tag{3-10}$$

When a gas mixture is given in volume fractions the partial pressure of each gas component can be determined by means of Boyle's law, from which it follows that at a constant temperature

$$p_iV=pV_i \quad \text{and} \quad p_i=p\frac{V_i}{V}=r_ip. \tag{3-11}$$

The partial pressure of each gas is equal to the product of the total pressure of the gas mixture by its volume fraction.

Equation (3-11) is used usually when calculating and testing the performance of heat installations. The volume fractions of the component gases are determined by means of special apparatus—gas analyzers.

Typical Questions and Examples to Chapter Three

1. What is meant by a mixture of gases?
2. Give the formulation of Dalton's law.
3. What is called partial pressure?
4. What is meant by the mass, volume and molar fractions?
5. What is partial, or reduced, volume?
6. How are the specific volume, density, molecular mass and the gas constant interrelated?
7. Why is the molecular mass of a gas mixture referred to as the mean molecular mass?

8. How can the mass composition of a gas mixture be expressed in terms of a volume composition and vice versa?
9. How can the gas constant of a gas mixture be determined by the known mass and volume fractions?
10. How is the partial pressure of a gas in a mixture determined from mass and volume fractions?
11. How is the mean molecular mass of a gas mixture determined?

Example 3-1. Determine the mean molecular mass of dry atmospheric air, assuming that it consists of 21 per cent of O_2 and 79 per cent of N_2 in volume fractions.

From Eq. (3-9) we have

$$\mu = r_1\mu_1 + r_2\mu_2 = 32 \times 0.210 + 28.016 \times 0.79 = 28.93.$$

Example 3-2. Determine the gas constant, density and partial pressures of the components of a gas mixture consisting of 20 mass fractions of air and one mass fraction of lighting gas. At the temperature of 273 K and the pressure, equal to 101 325 N/m², the density of the lighting gas is 0.52 kg/m³.

The gas constant of the lighting gas is determined from Clapeyron's equation

$$R = \frac{101\,325}{0.52 \times 273} = 714 \text{ J/kg·deg.}$$

The gas constant of air is 287.04 J/kg·deg.

The gas constant of the gas mixture is determined from Eq. (3-3)

$$R = g_1R_1 + g_2R_2 = 287.04 \times 20/21 + 714 \times 1/21 = 306.3 \text{ J/kg·deg.}$$

The density of the gas mixture is determined from Clapeyron's equation

$$\varrho = \frac{p}{RT} = \frac{101\,325}{306.30 \times 273} = 1.21 \text{ kg/m}^3.$$

The partial pressure of air is found from Eq. (3-11)

$$p_1 = pg_1\frac{R_1}{R} = 101\,325 \times \frac{20}{21} \times \frac{287.04}{306.3} = 90\,100 \text{ N/m}^2.$$

The partial pressure of lighting gas is equal to

$$p_2 = pg_2 = \frac{R_2}{R} = 101\,325 \times \frac{1}{21} \times \frac{714}{306.30} = 11\,225 \text{ N/m}^2.$$

CHAPTER FOUR

REAL GASES

4-1. Properties of Real Gases

Real gases differ from ideal ones in that the molecules of these gases have finite volumes and the forces of interaction, existing between the molecules, are of an electromagnetic and quantum nature. These forces of interaction exist between any molecules in any conditions and they diminish with increasing distance between the molecules. When the intermolecular distance gets small the forces of attraction decrease drastically and turn into repulsive forces, acquiring very great magnitudes.

Due to the presence of the intermolecular forces and also to the finite molecular volumes, the laws of ideal gases can never be strictly applied to real gases.

In practical calculations of various properties of real gases, the ratio $pv/RT=C$, which has been termed *compressibility factor*, is widely applied.

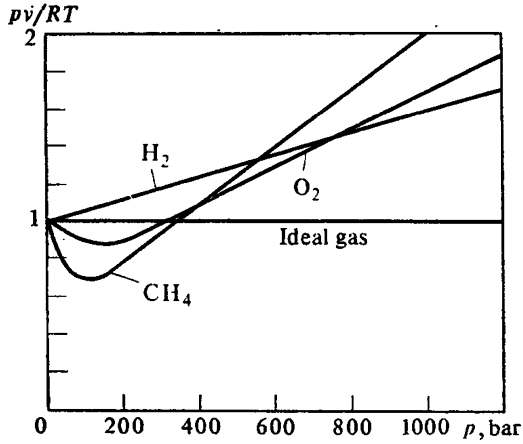


FIG. 4-1

(This quantity is not the thermodynamic compressibility coefficient considered in Sec. 4-3.)

Since for ideal gases $pv=RT$ and $C=1$ in any conditions, the compressibility factor expresses the departure of the properties of a real gas from these of an ideal one. For a real gas the factor C can be assumed to be greater or smaller than unity, depending on pressure and temperature,

and is practically equal to unity only at very low pressures and high temperatures.

In Fig. 4-1 the compressibility factor C is plotted as a function of pressure for some gases at temperature $t=0$ °C. A rise in pressure and drop in temperature, an increase in the concentration of gas molecules and a shorter distance between them, augments the departure of the properties of a real gas from those of an ideal one. It follows from Clapeyron-Mendeleyev's equation that at any constant temperature the dependence of the product pv on p must be represented on a pv-p diagram by a straight line parallel to the x-axis on which pressure is plotted. Actually, the isotherms of all gases are curves even in the region of not very high pressures, and at pressures from 200 bar and higher, the curves rise rather steeply.

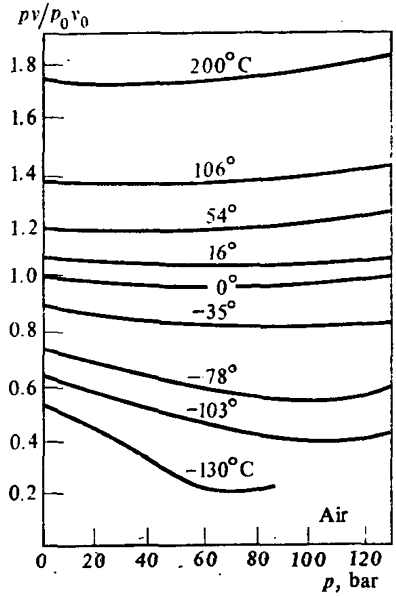


FIG. 4-2

It can be seen from Fig. 4-2 that for air, in the low pressure region, when $p\to 0$, the ratio pv/p_0v_0* tends to its limit $pv/p_0v_0=\text{const}$. It follows that for small values of p and great values of v the product pv changes very little and remains almost constant. Consequently, the greater the rarefaction, the greater the accuracy with which Clapeyron-Mendeleyev's equation is true for any real gas.

The temperature corresponding to the isotherm whose minimum lies on the y-axis is called *Boyle's temperature*. The isotherm initiating at the Boyle point will first run as a straight line, parallel to the abscissa, i.e. along this straight line the law $pv/p_0v_0=\text{const}$ is strictly observed. All isotherms beginning above the Boyle temperature appear as rising curves. For air Boyle's temperature is equal to 54 °C.

Thus, the properties of real gases differ materially from the properties of ideal gases both quantitatively and qualitatively. That is why all results obtained for real gases by applying ideal gas laws to them should be considered as approximate results, holding true only at very great rarefactions ($p\to 0$).

The difference between the properties of any real gas and those of an ideal one has compelled scientists to work out and derive new equations of state which would relate the parameters p, v and T and would make it

* Here p_0 and v_0 denote the pressure and specific weight of air under standard (physical) conditions, and the ratio pv/p_0v_0—the so-called Amagat number.

possible to calculate some properties of gases in various conditions, without resorting to direct measurements which involve great expenditures and are not always possible.

For the past 100 years a considerable number of different equations of state for real gases have been suggested, but none of them could be applied to solve general-case problems.

The development of the kinetic theory of gases has made it possible to work out an exact equation* of state for real gases in the following form

$$pv = RT\left[1 - \sum_{\nu=1}^{\infty} \frac{\nu}{\nu+1} \frac{B_\nu}{v^\nu}\right],$$

where the coefficients B_ν to the power $1/v$, called the *virial coeffcients*, are expressed in terms of the potential energy of the molecular interaction of the given gas at temperature T, and $\nu = 2, 3, 4, \ldots, n$ is the ordinal number of the virial coefficient.

However, the derived equation cannot be used in this general form for calculating processes involving real gases.

In some special cases, when the law governing the variation of the potential energy of molecular interaction as a function of intermolecular distance (the so-called potential curve) is known and certain experimental data are available, it is possible to calculate an equation for different real gases with their properties varying in a rather wide interval. The calculation of the virial coefficients involves great difficulties, and therefore usually only the first two of them are calculated. Then the calculated equation acquires the following appearance

$$pv = RT\left(1 - \frac{A}{v} - \frac{B}{v^2}\right),$$

where A and B are the first and second virial coefficients which are functions of temperature only.

At the present time equations of this kind have found wide application in calculating the properties of real gases.

The behaviour of a real gas is most simply and qualitatively reflected by the van der Waals equation which is derived from the general Mayer-Bogolyubov's equation of state by neglecting in the right-hand side of the general equation all terms containing $1/v$ to the second and greater power.

4-2. The van der Waals Equation of State

The van der Waals equation of state was derived as for one of the first attempts to describe analytically the properties of real gases. This equation demonstrates the qualitative characteristics of real gases and their distinction from ideal ones.

* The equation was derived by the Soviet mathematician N. N. Bogolyubov and the American physicist J. E. Mayer and was, therefore, named after them.

As was already mentioned, real gases differ from ideal ones in the forces of interaction between molecules and in the volumes of the molecules. The forces of intermolecular interaction are very great in solids and liquids and sufficiently great in gases that are close to a change from the gaseous into the liquid state.

Consequently, the farther a real gas from transformation into liquid, and the greater the distance between molecules, the smaller the forces of molecular interaction and the closer the state of the real gas to that of an ideal one. And, conversely, the closer the state of a gas to the liquid phase, the greater the forces of molecular interaction and the greater the deviation of its properties from those of an ideal gas. Thus, while studying the properties of real gases, account should be taken of the forces of molecular interaction and of the volume of the molecules.

As a first approximation van der Waals introduced two corrections into his equation, which take into account the departure of a real gas from an ideal one.

Let us consider the first correction, depending on the volume of molecules.

Clapeyron's equation can be presented in the following form

$$v = RT/p.$$

With increasing pressure the volume v will diminish, and if $p \to \infty$, then $v \to 0$. This conclusion fully agrees with the definition of an ideal gas according to which the molecules occupy an infinitely small volume.

But if we consider a real gas whose molecules occupy a finite volume v^*_{mol}, and allow for the volume of the voids existing between molecules in condition of full molecule-molecule packing, v_{void}, then the free volume for molecular motion shall be equal to $v-b$, where $b = v_{mol} + v_{void}$.

The quantity b represents the smallest volume to which the gas can be compressed.

In these conditions Clapeyron equation takes another appearance

$$v - b = RT/p.$$

If in the obtained relationships the pressure p increases and tends to infinity, then the free volume $v-b$ tends to zero or $v \to b$, i.e. at $p \to \infty$ the volume of gas tends to the value b that depends on the own volume of the molecules. For each real gas the value b takes a definite numerical value.

Inasmuch as Clapeyron equation determines the pressure of an ideal gas as

$$p = RT/v,$$

* It is assumed then that the molecules of a real gas are non-deforming balls (spheres).

and the pressure of a real gas, taking into account the quantity b

$$p=RT/(v-b),$$

at the same temperature the pressure of real gases shall be higher.

This can be attributed to the fact that the free volume of a real gas is smaller than that of an ideal one and, consequently, the free-path length is also smaller, resulting in a greater number of impacts of the molecules of a real gas with the walls of the confining, i.e. resulting in rise in pressure.

The second correction introduced into the equation of state accounts for the effect of forces of molecular interaction.

In an ideal gas the molecules are practically in free motion and their impacts with the walls of the vessel are in no way restricted since there are no forces of molecular interaction.

In a real gas, in the presence of forces of molecular interaction, there will be a smaller number of impacts with the walls of the vessel, due to the fact that the molecules positioned at the walls are attracted inside the vessel by the adjacent molecules. Consequently, compared with an ideal gas, the pressure exerted by a real gas will also be smaller by Δp, which is the correction for the pressure, accounting for the forces of molecular interaction. This correction Δp is directly proportional both to the number of attracted and the number of attracting molecules, or directly proportional to the square of density of the gas, or inversely proportional to the square of its specific volume

$$\Delta p=a\varrho^2=a/v^2$$

where a is the proportionality factor whose numerical value is definite for each gas, independent of the parameters of state.

Introducing the second correction, we obtain

$$p=\frac{RT}{v-b}-\Delta p \quad \text{or} \quad p=\frac{RT}{v-b}-\frac{a}{v^2}.$$

As a result, the van der Waals equation takes the form

$$(p+a/v^2)(v-b)=RT. \tag{4-1}$$

Equation (4-1) was published by van der Waals in 1873.

The quantity a/v^2 is called the *internal pressure:* it is very great for liquids (for water at a temperature of 293 K $a/v^2\approx 10\,800$ bar); for gases the internal pressure is comparatively small and depends on gas pressure and temperature.

The van der Waals equation reflects qualitatively the true behaviour of real substances in the liquid and gas state. It is not applicable to two-phase states.

For 1 kmole of gas the van der Waals equation takes the form

$$(p+a_\mu/v_\mu^2)(v_\mu-b_\mu)=8314.2T.$$

For a real gas described by the van der Waals equation of state, the main partial derivatives of parameters acquire the following appearance

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}$$

$$\left(\frac{\partial T}{\partial p}\right)_v = \frac{v-b}{R}.$$

4-3. Analysis of the van der Waals Equation

If in the van der Waals equation

$$(p + a/v^2)(v-b) = RT$$

we remove the brackets and arrange the obtained quantities in a decreasing v sequence, we obtain an equation of the third order in the specific volume of gas

$$pv^3 - (bp + RT)v^2 + av - ab = 0$$

As is generally known from mathematics, with given values of p and T, such an equation has three roots, corresponding to the three possible cases: (1) all three roots are different and real; (2) all three roots are real and equal to one another; and (3) one root is real and two are imaginary. In the third case only the real root has a real value, since the imaginary roots have no physical meaning.

Plotted on a p-v diagram, the isotherms described by the van der Waals equation will be represented by curves as depicted in Fig. 4-3. An analysis of the curves shows that at comparatively low temperatures the curves have in the middle a sigmoid section with a maximum and minimum, with the sigmoid section of an isotherm being the shorter the higher the temperature. The straight line AB crossing an isotherm of this type gives three real values of the specific volume at the points A, R and B, i.e. these isotherms correspond to the first solution of the van der Waals equation yielding three different real roots. The largest root, equal to the specific volume at point B pertains to the vapour (gas) state, and the smallest root (at point A)—to the liquid state. Inasmuch as, as was mentioned above, the van der Waals equation cannot be used in principle to describe two-phase states, it points (in the form of the sigmoid) to a continuous liquid-vapour phase change at the given temperature. In fact, numerous experimental studies have shown that the change from the liquid to the vapour phase passes through two-phase states of substance which are mixtures of liquid and vapour. At a given temperature the liquid-vapour phase change occurs at a constant pressure.

For extra pure substances the sections of the sigmoid AQ and DB can be reproduced in practice. The curve AQ corresponds to the metastable state of superheated liquid, and the section DB—to the metastable state of supercooled vapour. As to the section QRD of the sigmoid curve, it cannot be realized, since it is in violation with the condition of thermodynamic

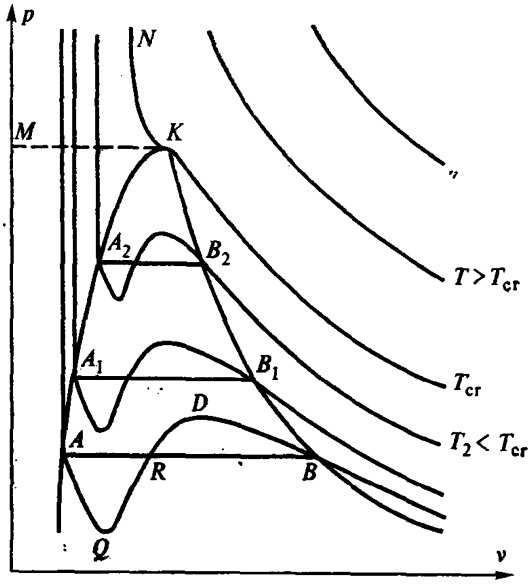


FIG. 4-3

stability, according to which for a homogeneous substance the partial derivative $(\partial p/\partial v)_T$ cannot exceed zero.

The process involving a liquid-vapour phase change is represented on the p-v diagram in Fig. 4-3 by the straight line AB, with point A corresponding to the state of boiling liquid, and point B—to the state of the so-called dry saturated vapour, i.e. to the state in which the process of the liquid-vapour phase change ended. The section of the isotherm located to the right of point B corresponds to the state of superheated vapour at that temperature.

At a definite temperature, referred to as the *critical*, the isotherm representing the van der Waals equation will have no sigmoid section. There is a point of inflection on this isotherm, and the tangent to this point must be horizontal. This corresponds to the second case of solving the van der Waals equation when all the three roots are real and equal to each other (Fig. 4-3, point K).

At temperatures above the critical ($T>T_{cr}$) the isotherms drop monotonically approaching a hyperbola-like form with rising temperature. At

these temperatures the third case of solving the van der Waals equation takes place, when one of the roots is real and two—imaginary. The line passing through points A, A_1, A_2, etc. is the locus of all boiling liquid states. Curve AK is called the lower *boundary curve*. Curve BK, correspondingly referred to as the upper *boundary curve*, is the locus of dry saturated-vapour states. Thus, for a real substance the p-v diagram can be divided into three characteristic regions: (1) the liquid state region, to the left of the lower boundary curve; (2) the region of liquid-vapour or two-phase states (of wet vapour), located between the lower and upper boundary curves; and (3) the superheated vapour region, to the right of the upper boundary curve and on top of the critical point. The liquid state region is arbitrarily restricted at the top by line KM which is a critical isobar (line of constant pressure equal to critical).

The Irish chemist T. Andrews was the first to construct in 1869 a p-v diagram for a real substance based on experimental studies devoted to isothermal compression of carbon dioxide, showing characteristic lines and regions on the diagram. That is why the p-v diagram of a real substance is often called *Andrews' diagram.*

Let us consider in a somewhat greater detail the concept of the critical state of substance.

The critical state of substance was first discovered by the Russian scientist D. Mendeleyev in 1861, who gave the critical temperature the name of *absolute boiling temperature* at which the surface tension in the liquid becomes equal to zero, i.e. the difference between the liquid and the vapour state of a substance (saturated vapour) vanishes.

Mendeleyev gave the following definition: "By the absolute temperature of boiling I mean the temperature at which the particles of liquid lose their adhesion (the rise in a capillary tube is zero, latent heat is equal to zero) and at which the liquid, irrespective of the magnitude of pressure and volume, wholly turns into vapour." Numerous experimental studies conducted with real gases have fully corroborated the existence of the critical point at which the difference between the vapour and liquid phases vanishes.

From an analysis of the van der Waals equation as applied to the critical state, we can obtain critical parameters in terms of the constants a and b of the van der Waals equation of state or determine the constants a and b when the critical parameters are known.

Considering that the van der Waals equation describes only qualitatively the behaviour of real substances, the constants a and b are usually calculated from experimental data.

The critical parameters can be related with the constants of the van der Waals equation, starting with the assumption that at the critical point the isotherm has a point of inflection and that the tangent to the point of inflection is horizontal. It follows from these conditions that the first partial derivative of pressure with respect to volume at a constant temperature,

$(\partial p/\partial v)_{T_{cr}}$, and also the second partial derivative $(\partial^2 p/\partial v^2)_{T_{cr}}$ at that point must be equal to zero. Then

$$(\partial p/\partial v)_{T_{cr}} = -RT_{cr}/(v_{cr}-b)^2 + 2a/v_{cr}^3 = 0; \tag{a}$$

$$(\partial^2 p/\partial v^2)_{T_{cr}} = 2RT_{cr}/(v_{cr}-b)^3 - 6a/v_{cr}^4 = 0, \tag{b}$$

where T_{cr} and v_{cr} are the temperature and specific volume at the critical point. Eq. (a) yields

$$RT_{cr}/(v_{cr}-b)^2 = 2a/v_{cr}^3, \tag{c}$$

and it follows from Eq. (b) that

$$2RT_{cr}/(v_{cr}-b)^3 = 6a/v_{cr}^4 \tag{d}$$

Upon transformation of equations (c) and (d) we obtain

$$v_{cr} = 3b. \tag{4-2}$$

Substituting the value of v_{cr} in equation (a), we get

$$T_{cr} = 8a/27Rb. \tag{4-3}$$

It follows from van der Waals equation that

$$p = RT_{cr}/(v_{cr}-b) - a/v_{cr}^2.$$

Substituting T_{cr} and v_{cr}, we find that

$$p_{cr} = a/27b^2 \tag{4-4}$$

where p_{cr} is the pressure at the critical point.

Having determined experimentally the values of T_{cr} and p_{cr}, it is possible to find the constants a and b

$$a = \frac{9}{8} RT_{cr} v_{cr} = \frac{27}{64} \frac{R^2 T_{cr}^2}{p_{cr}} \tag{4-5}$$

and

$$b = \frac{1}{3} v_{cr} = \frac{1}{8} \frac{RT_{cr}}{p_{cr}} \tag{4-6}$$

The van der Waals equation can be expressed in reduced parameters of state. Substituting in the van der Waals equation the variables p, v and T with the relative quantities

$$v/v_{cr} = \varphi, \quad p/p_{cr} = \pi \quad \text{and} \quad T/T_{cr} = \tau,$$

referred to as the *reduced volume, pressure and temperature*, and the values of a, b and R, expressed in terms of the critical parameters, we obtain a new equation in the following form

$$(\pi + 3/\varphi^2)(3\varphi - 1) = 8\tau.$$

The above equation is called a *reduced equation.* It does not include quantities characterizing a given substance. Therefore, the equation is true for any substance obeying the van der Waals equation. The states of substances at which the values of π, φ and τ are the same are referred to as *corresponding states.*

At the critical point all the three reduced parameters are the same, equal to unity, and the critical states of all substances are corresponding states.

If two substances have the same two of the three reduced parameters of state, then the third reduced property of state will also be the same for the substances involved, and the substances will be in the corresponding states. This phenomenon is called the *law of corresponding states,* used to determine the properties of a substance, if the properties of another substance which is in a state corresponding to that of the first substance, are known. This method of determining the properties of a substance is called the *method of thermodynamic similarity.*

From the relationships for the critical point, derived from the van der Waals equation, it follows that

$$RT_{cr}/p_{cr}v_{cr}=8/3=2.67.$$

This ratio, denoted by K_{cr}, is called the *critical coefficient.* It must be the same for all thermodynamically similar substances satisfying the van der Waals equation, but experimental studies have shown the values of K_{cr} for various substances to differ considerably from the constant value (Table 4-1). This confirms once more that the van der Waals equation

TABLE 4-1

Gas	Chemical symbol	Constants		Critical parameters			$K_{cr}=RT_{cr}/p_{cr}v_{cr}$
		a, bar·cm⁶/kg	b, cm³/kg	Temperature T_{cr}, K	Pressure p_{cr}, bar	density ϱ_{cr} kg/m³	
Nitrogen	N_2	1.345×10^6	38.6	126.1	32.8	311	3.54
Argon	Ar	1.333×10^6	32.3	150.8	52.0	531	3.54
Water vapour	H_2O	5.38×10^6	30.6	647.3	221.6	325	4.60
Hydrogen	H_2	0.241×10^6	26.6	33.3	12.5	31	3.49
Helium	He	0.0323×10^6	23.4	5.3	2.2	69	3.48
Oxygen	O_2	1.323×10^6	31.9	154.4	49.8	430	3.56
Ammonia	NH_3	4.12×10^6	37.3	408.7	111.8	235	4.26
Methane	CH_4	2.21×10^6	42.8	190.8	33.9	162	3.56
Carbon monoxide	CO	1.43×10^6	39.4	133.6	34.8	311	3.66
Carbon dioxide	CO_2	3.53×10^6	42.8	304.1	73.8	460	3.66
Chlorine	Cl_2	6.37×10^6	56.2	417.0	74.5	573	3.74
Ethylene	C_2H_4	4.4×10^6	57.2	282.7	50.0	220	3.33

describes only the qualitative peculiarities of the properties of real substances in the gaseous state.

Before the critical state of the substance was discovered attempts were made to liquefy gases only by increasing pressure, but since the experiments were conducted at room temperature, these attempts proved fruitless.

It has been shown experimentally that to liquefy a gas, it is first necessary to cool it to a temperature below the critical and only then any gas can be liquefied by compressing it isothermally.

4-4. Vukalovich-Novikov's Equation of State for Real Gases

When applied to high density gases the van der Waals equation gives considerable errors due to the fact that in deriving the equation no account was made of some additional physical phenomena and above all of the so-called power association and dissociation of molecules.

In addition, it was shown experimentally that the factors a and b in the van der Waals equation cannot be constant quantities, and must depend on temperature and pressure in an intricate way.

However, the attempts undertaken by many scientists to correct the van der Waals equation by introducing into it additional relations taking account of the variation of a and b have failed to widen materially the field of applicability of the equation.

The Soviet scientists M. P. Vukalovich and I. I. Novikov suggested in 1939 a new universal equation of state for real gases which differs qualitatively from the van der Waals equation. In deriving their equation, the authors allowed for the above mentioned phenomenon of power association of molecules under the effect of the forces of molecular interaction.

The association phenomenon involves the formation of complexes consisting of two, three, four or a greater number of individual molecules which, entering the groups of complex particles preserve their individual properties and do not realize fully all their degrees of freedom. Consequently, by molecular association is meant a simple, mechanical association of two, three, four or more molecules into one compound particle which behaves in some respects as an independent gas particle. The totality of homogeneous gas particles, formed as a result of molecular association, can be considered as an ordinary gas. But any real gas is considered to be a mixture of several gases whose particles are single, double, triple, etc. groups of molecules. These gases interact continuously with each other, and each of them obeys with sufficient accuracy the van der Waals equation. Applying to such gases the mass action law, assuming association to lead to the formation of groups comprising two, three and four molecules M. P. Vukalovich and I. I. Novikov derived the equation of state which was used as a basis for the first Soviet steam tables published by M. P. Vukalovich in 1940. Later on this equation was made much more precise and ifs field of application considerably widened. In the simplest form, when only twin molecular

complexes are taken into account, Vukalovich-Novikov's equation has the following appearance

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT\left(1-\frac{C}{vT^{\frac{3+2m}{2}}}\right),$$

where a and b are van der Waals constants; C and m are constants determined on the basis of experimental data.

4-5. Partial Derivatives of Parameters of State. Thermal Coefficients

If the equation of state is known, each parameter of state can be expressed as a function of the two other parameters, i.e.

$$p=f_1(v,\ T);\quad T=f_2(p,\ v);\quad v=f_3(p,\ T)$$

The total differentials of these quantities will be

$$\left.\begin{aligned} dp&=\left(\frac{\partial p}{\partial v}\right)_T dv+\left(\frac{\partial p}{\partial T}\right)_v dT,\\ dT&=\left(\frac{\partial T}{\partial p}\right)_v dp+\left(\frac{\partial T}{\partial v}\right)_p dv,\\ dv&=\left(\frac{\partial v}{\partial p}\right)_T dp+\left(\frac{\partial v}{\partial T}\right)_p dT. \end{aligned}\right\} \tag{4-7}$$

The partial derivatives at the differentials dp, dT and dv are mutually reciprocal quantities in pairs and, in accordance with differential calculus, they are interrelated as follows

$$\left(\frac{\partial v}{\partial p}\right)_T\left(\frac{\partial p}{\partial v}\right)_T=1;\quad \left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial T}\right)_p=1;\quad \left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial p}\right)_v=1.$$

Hence, three of them shall be independent partial derivatives, the following are chosen as independent partial derivatives

$$\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial p}\right)_T \quad \text{and} \quad \left(\frac{\partial v}{\partial T}\right)_p.$$

These partial derivatives are present in the equation for thermal coefficients—of compression, expansion and thermal elasticity (pressure) that can be determined by experiment.

The indicated partial derivatives are not independent. Each of them can be expressed as a function of the other two.

If equation

$$dp=\left(\frac{\partial p}{\partial v}\right)_T dv+\left(\frac{\partial p}{\partial T}\right)_v dT$$

is considered at $p=\text{const}$, then

$$\left(\frac{\partial p}{\partial v}\right)_T dv_p+\left(\frac{\partial p}{\partial T}\right)_v dT_p=0,$$

or

$$\left(\frac{\partial p}{\partial v}\right)_T+\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p=0,$$

whence

$$\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p=-\left(\frac{\partial p}{\partial T}\right)_v=-\frac{1}{\left(\frac{\partial T}{\partial p}\right)_v},$$

or

$$\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v=-1.$$

The expression thus obtained can be referred to as the differential equation of state, from which it follows that

$$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v=-\frac{1}{\left(\frac{\partial p}{\partial v}\right)_T},$$

or

$$\left(\frac{\partial v}{\partial p}\right)_T=-\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_v}. \tag{4-8}$$

Relationship (4-8) can be used to relate the isothermal coefficient of compression β_t, the thermal coefficient of expansion of a body α_p and the coefficient of thermal pressure γ_t. These quantities, measured with sufficient accuracy in experimental studies, are of essential importance for the characteristic properties of real substances.

The ratio of the partial derivative $(\partial V/\partial p)_T$ to volume V characterizes the rate of change in volume with increasing pressure at a constant temperature. This ratio is called the isothermal compressibility coefficient

$$\beta_T=-(1/V)(\partial V/\partial p)_T. \tag{4.9.}$$

The minus sign in the right-hand side of Eq. (4-9) serves to make β_T a positive quantity, for the partial derivative $(\partial V/\partial p)_T$ is always negative.

The ratio of the partial derivative $(\partial V/\partial T)_p$ to volume V characterizes the rate of change in volume upon heating, when pressure remains constant. This ratio is called the coefficient of thermal expansion of a body

$$\alpha_p=(1/V)(\partial V/\partial T)_p. \tag{4-10}$$

The ratio of the partial derivative $(\partial p/\partial T)_V$ to pressure p characterizes the rate of change in pressure with rising temperature, if the volume of the body remains constant.

This ratio is referred to as the coefficient of thermal pressure

$$\gamma_t=(1/p)(\partial p/\partial T)_V \tag{4-11}$$

Substituting the values of the partial derivatives into Eq. (4-8), we obtain

$$-\beta_T=-\alpha_p/\gamma_T p,$$

whence the coefficient of thermal pressure is equal to

$$\gamma_T=\frac{1}{p}\frac{\alpha_p}{\beta_T}. \tag{4-12}$$

The coefficients α_p and β_T are determined by experiment. For ideal gases

$$\alpha_p=\beta_T=1/T.$$

Typical Questions to Chapter Four

1. What distinguishes real gases from ideal ones?
2. What is meant by the coefficient of compressibility?
3. Write the equation of state of real gases with virial coefficients.
4. What is the basis in deriving the van der Waals equation?
5. What is the meaning of the constant b in the van der Waals equation?
6. What quantity is referred to as the internal pressure of a gas?
7. Write the van der Waals equation for 1 kg of gas.
8. Analyze the van der Waals equation.
9. Explain the meaning of the roots of the volume of substance in different states obtained from the van der Waals equation.
10. Who was the first to prove the existence of the critical point?
11. How are the constants a and b in the van der Waals equation calculated in terms of critical parameters of state?
12. Under what conditions can gases be liquefied?
13. Write the van der Waals equation in reduced parameters.
14. State the law of corresponding states.
15. Explain the meaning of molecular association.
16. What was used as the basis in deriving the Vukalovich-Novikov equation of state for real gases?
17. What is meant by the isothermal compressibility coefficient?
18. What is meant by the coefficient of thermal expansion?
19. What is meant by the coefficient of thermal pressure?
20. How are these coefficients interrelated?

CHAPTER FIVE

THE FIRST LAW OF THERMODYNAMICS

5-1. Law of Conservation and Conversion of Energy

The first law of thermodynamics is a special case of the fundamental general law of conservation and conversion of energy as applied to thermal phenomena proceeding in thermodynamic systems.

The law of conservation and conversion of energy states that in an isolated thermodynamic system the sum of all kinds of energy is a constant quantity. It follows from the law that a decrease in some kind of energy in one system, consisting of one or a great number of bodies, must be accompanied by an increase in energy in another system of bodies.

The conversion of mechanical motion into heat has been known to man from ancient times, but the inverse conversion of heat into mechanical work in heat engines was realized in practice only in the second half of the 18th century. And although the first attempts to convert heat into mechanical work had been undertaken as far back as B.C., they have not influenced in any way the creation of the heat engine. So, for instance, in the first century B.C. Heron of Alexandria invented a ball that rotated under the action of reactive forces created by the water vapour (steam) that escaped from the ball when the latter was heated. At the beginning of the 17th century the Italian scientist Bronco created an apparatus in which the kinetic energy of steam was utilized to rotate a wheel set on a vertical shaft.

At the beginning of the 18th century the French scientist D. Papin attempted to create a reciprocating steam engine. However, it was only in 1766 that such a machine was created by the Russian inventor I. I. Polzunov.

Thus, at the end of the 18th century the process of conversion of heat into mechanical work was realized, but without any theoretical calculations and substantiation. The general statement of the law of conservation and conversion of energy was given by the great Russian scientist M. V. Lomonosov who, however, was unable to establish the equivalence of various forms of motion of matter and relate them qualitatively, since the actual data required for this purpose was not available to him.

Only a century after Lomonosov, in the first half of the 19th century, did science come close to the discovery of the law of conservation and conversion of energy and of the equivalence of heat and work.

In 1842 J. R. Mayer established experimentally a direct proportionality

between heat Q spent and work L obtained and determined the quantitative relation between them, viz.

$$Q=AL,$$

where A is a constant referred to as the thermal equivalent of work. The thermal equivalent of unit work is a dimensional quantity and depends on the system of units chosen to measure heat and work. If heat and work are measured in the same units (joules), then the proportionality factor is equal to unity and

$$Q=L. \tag{5-1}$$

The relationship derived by Mayer states not only the equivalence of heat and work, i.e. the quantitative constancy of energy, but also the change in the quality of energy itself.

In his work "Dialectics of Nature" Engels wrote that the quantitative constancy of motion was already expressed by Descartes and almost in the same expressions as by Clausius and Mayer now, whereas the conversion of the forms of motion was discovered only in 1842, and it was this, and not the law of the qualitative constancy, that was new.

And further Engels wrote that any form of motion proved to be capable of and subject to conversion into any other form of motion. Coming to this form, the law reached its last expression.... It is the absolute law of nature.

In 1843 the English scientist J. Joule, and in 1844 the Russian academician F. Lenz established the relation between electric energy and heat. They proved the equivalency of electric work and heat. In elementary physics this law is known as the Joule-Lenz law.

In 1847 H. Helmholtz published his work "On the Conservation of Force" in which he treated scientifically the law of conservation of energy.

In 1850 R. Clausius published a paper entitled "On the Motive Force of Heat" which gave a mathematical substantiation of the law of conservation of energy and also an analysis of the peculiarities of heat in ideal and real processes as well as an explanation not only of the quantitative, but also of the qualitative content of the discovered law.

Thus, the law of conservation and conversion of energy, which was discovered by M. V. Lomonosov, but failed to find wide application during his lifetime, gained an absolute recognition in the second half of the 19th century.

5-2. Internal Energy

By the internal energy of a gas is meant the entire energy contained in a body or system of bodies. This energy can be represented as the sum of individual kinds of energy: the kinetic energy of molecules, comprising the energy of their translational and rotational motion, and also of the oscillatory motion of atoms in the molecule; electron energy; nuclear

energy; the energy of interaction between the nucleus of a molecule and the electrons; the potential energy or the energy of molecules placed in some external field of forces; the energy of electromagnetic radiation. The internal energy of a body is equal to

$$U^* = U_{kin} + U_{pot} + U_0,$$

where U_{kin} = internal kinetic energy of molecules;
U_{pot} = internal potential energy of molecules;
U_0 = integration constant.

The internal kinetic energy can be subdivided into the following components

$$U_{kin} = U_{kin\,tr} + U_{kin\,rot} + U_{os},$$

where $U_{kin\,tr}$ = the kinetic energy of translational molecular motion;
$U_{kin\,rot}$ = the kinetic energy of rotational motion of molecules;
U_{os} = the energy of oscillatory motion of atomic nuclei in respect to each other.

The quantity U_0 is the zero energy or the internal energy at the absolute zero temperature. As is generally known, at $T=0$ the thermal motion of molecules and of atoms ceases, but the motion of particles inside the atoms continues. For instance, the motion of electrons in atoms is not thermal and it takes place at any temperature, including the temperature $T=0$. Since it is impossible to determine the absolute value of internal energy by means of thermodynamic methods, in conducting a thermodynamic analysis of a system we have to deal not with absolute values of internal energy, but with the change in internal energy resulting from the processes occurring in the system, that is why the solution of most thermodynamic problems does not require the knowledge of U_0 and it is usually assumed to be zero.

Engineering thermodynamics is concerned only with processes in which the kinetic and the potential components of internal energy undergo a change. Therefore, for ideal gases the concept of internal energy will henceforth embrace the kinetic energy of molecular motion and the energy of oscillatory motions of atoms, and for real gases, in addition, the potential component of energy associated with the presence of forces of molecular interaction and depending on the distance between molecules.

The internal energy can be measured from any arbitrary zero. Thus, for instance, for ideal gases at a temperature $t_0=0$ °C the internal energy is assumed to be equal to zero.

Inasmuch as the kinetic energy component of internal energy is fully determined by the temperature of a body, and its potential component

* The total internal energy of a body is usually denoted by U(J) and the specific internal energy, corresponding to 1 kg, by *u* (J/kg).

depends, in addition, on the specific volume (the distance between molecules) at a given temperature, the total internal energy will be a function of two parameters and, for a body in a given state will be of a definite value.

These values, as was stated above, are called the *parameters* or *functions of state*. Hence, while being a function of state, the internal energy is at the same time an unambiguous, continuous and finite function of state of a system.

The internal energy is an additive or extensive property, since its magnitude depends on the mass of the body. Reduced to 1 kg, the internal energy of a complex system is equal to the sum of the internal energy of system components, i.e.

$$u=u_1+u_2+\ldots+u_n=\sum_1^n u_i.$$

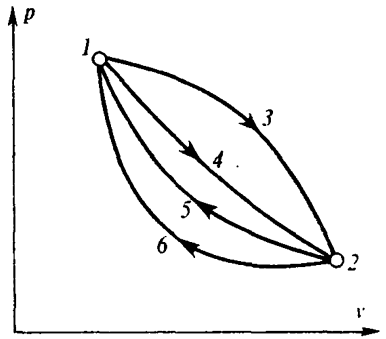


FIG. 5-1

It follows from the law of conservation of energy that a thermodynamic system can have in each of its states only one value of internal energy. Should we assume that in a given state a system can have different amounts of internal energy, we could use this difference in internal energies without changing the state of the system. Such an assumption is in contradiction with the law of conservation of energy. Therefore, the change in the internal energy of a gas is independent of the nature and path of a process, being fully determined by the given initial and final states of the system

$$u_2-u_1=f(p_2, v_2, T_2)-f(p_1, v_1, T_1) \qquad (5\text{-}2)$$

This is illustrated vividly in Fig. 5-1. In the course of all processes

$$(3)\int_1^2 du=(4)\int_1^2 du=(5)\int_1^2 du=-(6)\int_1^2 du=(6)\int_1^2 du$$

the change in internal energy is the same.

In cyclic processes the change in internal energy is equal to zero

$$u_2-u_1=\oint du=0$$

The increment of du, just as of any parameter, is a total differential. Since the state of a gas is fully determined by the basic properties of state, the internal energy can be presented as a function of any two properties of state

$$u=f(T, v); \quad u=f_1(T, p); \quad u=f_2(p, v),$$

or the total differentials of internal energy

$$\left.\begin{aligned} du&=(\partial u/\partial T)_v\,dT+(\partial u/\partial v)_T\,dv,\\ du&=(\partial u/\partial T)_p\,dT+(\partial u/\partial p)_T\,dp,\\ du&=(\partial u/\partial p)_v\,dp+(\partial u/\partial v)_p\,dv. \end{aligned}\right\} \tag{5-3}$$

The internal energy of an ideal gas, in which there are no forces of molecular interaction, does not depend on volume or pressure, $(\partial u/\partial v)_T=0$ and $(\partial u/\partial p)_T=0$, and depends only on temperature, $u=f(T)$.

Consequently, the derivative of the internal energy of an ideal gas with respect to temperature is a total derivative

$$(\partial u/\partial T)_p=(\partial u/\partial T)_v=du/dT.$$

This was proved by Joule who conducted in 1845 the following experiment: two vessels, interconnected by means of a pipe and a valve (Fig. 5-2),

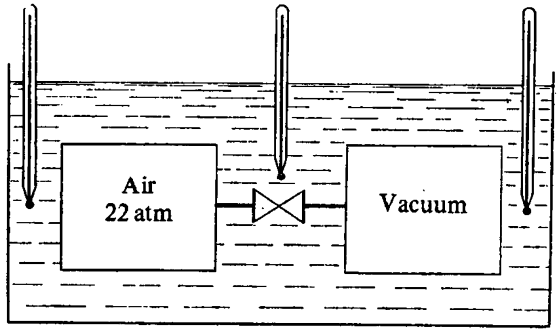


FIG. 5-2

were placed in a calorimeter filled with water. The first vessel contained air under pressure and the other vessel was evacuated. The temperature of the entire apparatus was measured with the aid of several thermometers.

After the temperature in the calorimeter remained constant and equal to the temperature of the air in the room for a long period of time, the valve separating the two vessels was opened and a fraction of air passed from the first vessel into the second.

A check on the temperature in the calorimeter showed that temperature remained constant, hence no heat was absorbed or released during the experiment ($Q=0$). No external work L was done by the air as it passed into the vessel with rigid walls, on condition that the vessel was evacuated ($L=0$).

In these conditions the internal energy of the air must also remain invariable. Since only temperature and internal energy remained invariable during the experiment, Joule came to the conclusion that the internal energy

of a gas only depends on temperature, $u=f(T)$. This conclusion holds true only for ideal gases.

Joule's conclusions can also be applied to real gases at high temperatures and low pressures with an account of experimental error. Therefore, for approximate calculations and under the stated conditions, the internal energy of real gases can be assumed to be a function of temperature only.

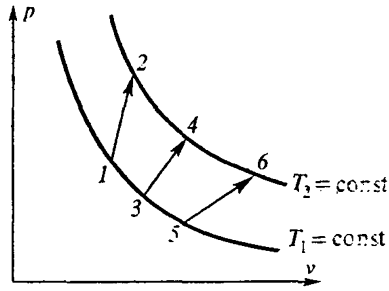


FIG. 5-3

If a number of arbitrary processes occurring with different initial and final volumes and pressures *1-2*, *3-4*, *5-6* are represented on a *p-v* diagram (Fig. 5-3) between the isotherms T_1 and T_2, the change in the internal energy of the gas undergoing these processes will be the same, i.e.

$$\Delta u=u_2-u_1=u_4-u_3=u_6-u_5=f(T_2)-f(T_1)$$

5-3. Analytical Expression of Work in a Process

The transfer of energy from one body to another, associated with a change in the volume of the working medium, with a displacement of the medium in the external space, or with a change in its position, is referred to as *work*. The performance of work always involves two or more bodies. The first body, performing work, transfers energy, the second body receives the energy transferred from the first one. As was already mentioned above, work is the macrophysical form of energy transfer from one body to another.

The work performed by a gas upon expansion depends on the change of the properties of state p, v and T.

To derive the equation of the work done by an expanding gas, let us consider a typical case—the work done in an equilibrium process at a constant pressure.

Let the space in a cylinder underneath the piston be filled with 1 kg of gas at a pressure p, equal in an equilibrium process to the pressure of the surrounding medium, and with a specific volume v_1 (Fig. 5-4); the piston area is F. If a certain amount of heat is transferred to the gas, it shall expand at a constant pressure and displace the piston to a new position at point *2*.

The force acting upon the piston is equal to pF; the piston is displaced through a distance S. It is known from elementary physics that the product of force by distance is equal to work. Then, the work performed by the gas is equal to

$$l=pFS,$$

but the product FS is the difference in specific volumes v_2-v_1, therefore

$$l=p(v_2-v_1)=p\,\Delta v. \qquad (5\text{-}4)$$

The elementary work dl, done by a system in an equilibrium process of change of state of a body with an infinitely small change in its volume, is determined by formula

$$dl = p\,dv. \tag{5-5}$$

The work l, done by a system upon a final change in its volume in an arbitrary equilibrium process, is depicted by the curve AB (Fig. 5-5) and is equal to

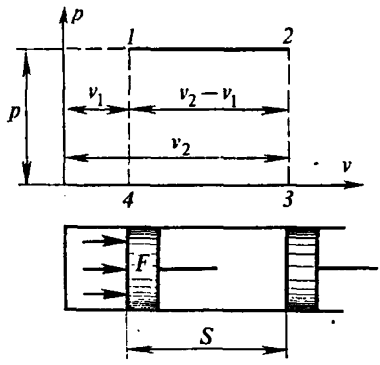


FIG. 5-4

$$l = \int_{v_1}^{v_2} p\,dv \tag{5-6}$$

Knowing the functional dependence of the properties p and v in a process, or the equation of the kind $p=f(v)$, we can determine analytically the work done in any equilibrium process within the limits indicated.

If a system performs work in the surrounding medium where the pressure is p', then the work done by the system upon expansion with an increase in volume by dv is equal to $dl=p'\,dv$, and when the volume undergoes a finite change from v_1 to v_2

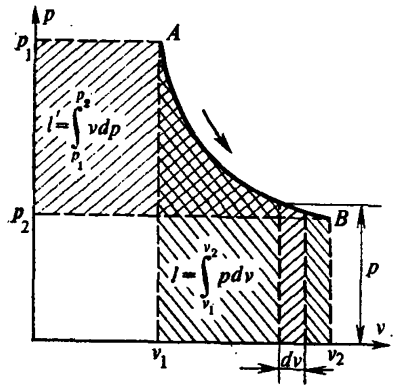


FIG. 5-5

$$l = \int_{v_1}^{v_2} p'\,dv. \tag{5-7}$$

For equilibrium processees the pressure $p'=p$.

It should be borne in mind that if a system expands in an evacuated space, when the pressure p' on the boundaries separating the system from the surrounding medium is equal to zero and no displacement of external bodies is observed, the work l is equal to zero, which follows from formula (5-7).

In addition to the work l associated with the change in volume and determined by formula (5-7), sometimes a working medium undergoes a change in the external kinetic energy without any change in volume [for instance, rotation of liquid with the aid of a stirrer, work performed against (or on) electric, magnetic and some other forces]. In a process

of this kind the integral $\int_{v_1}^{v_2} p'\,dv=0$, since $dv=0$. This work, performed by an external source, is denoted by l_v.

Consequently, in the general case the work of a system is the sum of the work of expansion and the work performed without a change in volume, i.e.

$$l=\int_{v_1}^{v_2} p'\,dv+l_v.$$

When a gas undergoes expansion not all the work of expansion can be put to useful purposes. Due to the increase in volume, a fraction of the work must be spent to displace the surrounding medium the pressure of which changes from p_1' to p_2'. Reduced to 1 kg of the expanding gas, this work of displacement (Fig. 5-6) is equal to

$$p_2'fh_2-p_1'fh_1$$

(where f is the area of the piston)

or

$$p_2'v_2-p_1'v_1.$$

Each quantity $p_2'v_2$ or $p_1'v_1$ represents the work that should be expended to force a gas with a volume v to flow into a surrounding medium which is at a pressure p'. Hence, the *useful*, or, as it is usually referred to, the *available work* l' is equal to the difference between the work of expansion and work of displacement, i.e.

$$l'=\int_{v_1}^{v_2} p'\,dv+l_v-(p_2'v_2-p_1'v_1).$$

Since

$$p'\,dv=(p'\,dv+v\,dp')-v\,dp'=d(p'v)-v\,dp',$$

then

$$\int_{v_1}^{v_2} p'\,dv=(p_2'v_2-p_1'v_1)-\int_{p_1'}^{p_2'} v\,dp'.$$

Then the available work or simply the availability

$$l'=-\int_{p_1'}^{p_2'} v\,dp'+l_v.$$

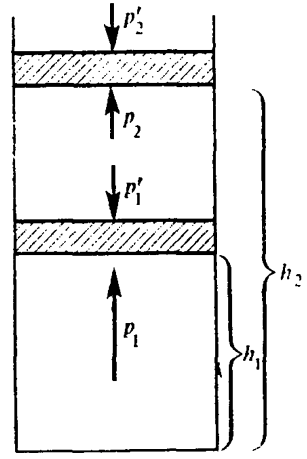


FIG. 5-6

Equations (5-4) and (5-5) show that l and dl have the same signs as Δv and dv, since absolute pressure p is a positive quantity.

If $v_2 > v_1$—the gas expands, then $\Delta v > 0$ and $dv > 0$, under these conditions the work done by the gas is positive.

If $v_2 < v_1$ the gas undergoes compression, then $\Delta v < 0$ and $dv < 0$, under these conditions the work done by the gas is negative.

If not 1 kg of gas but m kg undergo a process of expansion, the equation of work due to a change in volume takes the form

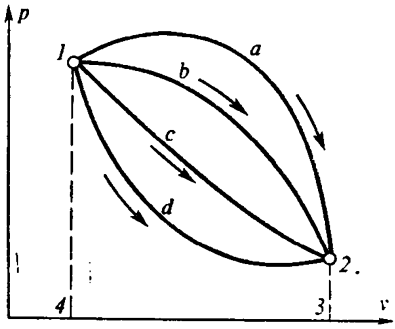


FIG. 5-7

$$L = m \int_{v_1}^{v_2} p\,dv.$$

The work due to a change in the volume of a gas (expansion) in an equilibrium process, determined by Eq. (5-6), is represented on a p-v diagram by the area ABv_2v_1 (Fig. 5-5) confined by the line of the process, extreme ordinates and the v-axis.

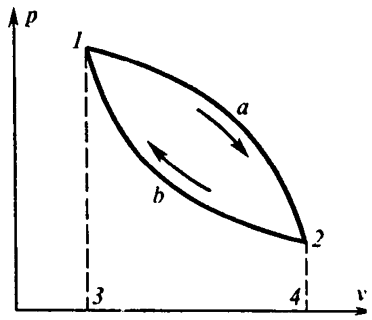


FIG. 5-8

$$l = \int_{v_1}^{v_2} p\,dv = l' + p_2v_2 - p_1v_1.$$

The available (useful) work of the gas, equal to $\int_{p_1}^{p_2} v\,dp$, is represented by area ABp_2p_1 confined by the line of the process, extreme abscissas and the p-axis (Fig. 5-5)

$$l' = l + p_1v_1 - p_2v_2.$$

It follows from the foregoing that the available (useful) work can both be greater and smaller than the work of expansion; it depends on the slope of the process curve on the p-v diagram.

It can be seen from Fig. 5-7 that the magnitude of the work of expansion (or compression) depends not only on the initial and final state of the body, but also on the nature of the process in the course of which the working medium passes from one state into another. All processes *1-a-2*, *1-b-2*, *1-c-2*, *1-d-2* have the same initial and final parameters, but different areas represent the work done in the process. Thus, for instance, the work done as the gas passes from state *1* into state *2* in the process *1-a-2* is represented by area *41a234*, and in the process *1-d-2*—by area *41d234*.

If a working medium undergoes a cyclic process, depicted on the *p-v* diagram in Fig. 5-8 by the closed curve *1-a-2-b-1*, then upon expansion along line *1-a-2* the working medium produces positive work, equal numerically to the area *1a2431*, and during compression proceeding along the curve of process *2-b-1* work is to be done on the working medium, equal numerically to the area *1b2431*, and this work will be negative. The difference between the two indicated areas represents the total work performed by the working medium undergoing one cyclic process or one cycle; this work will be equal numerically to the area *1-a-2-b-1*.

5-4. Reversible and Irreversible Processes

Let us consider the equilibrium process of expansion of gas *A-B* (Fig. 5-9) which has passed in the course of expansion all the equilibrium states *A, 1, 2, 3, n, B*. The work of expansion produced in this process is represented to a certain scale by area *ABCD*. For the working medium to return into its initial state (into point *A*), a reversed process must be initiated from point *B*, a process of compression. If the external pressure exerted on the piston is increased by *dp*, the piston shall move through an infinitely small distance and compress the gas in the cylinder to the pressure of the surrounding medium, equal to $p+dp$. With a further increase in pressure by *dp* the piston shall displace again through an infinitely small distance and the gas shall be compressed to a new pressure of the surrounding medium. During all the subsequent increases in the external pressure by *dp*, the gas, being compressed in the course of the reverse process, will pass in succession through all the equilibrium states of the forward process *B, n, 3, 2, 1, A* and shall return into the state characterized by point *A*. The work expended in the reverse process of compression (area *BACD*) shall be equal to the work of expansion done in the forward process (area *ABDC*). Under these conditions all points of the forward process shall coincide with the points of the reverse process. Processes that occur in the forward and reverse directions without any residual changes both in the working medium and in the surroundings are called *reversible*. Consequently, *any equilibrium thermodynamic process* of change of state of a working medium will always be a *reversible thermodynamic process*.

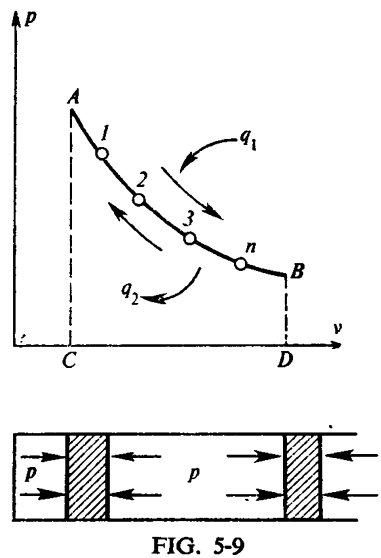


FIG. 5-9

Any thermodynamic process that passes through non-equilibrium states is called an *irreversible thermodynamic process*. After irreversible processes have taken

place in the forward and backward directions, a thermodynamic system does not return into the initial state without energy transfer from the surrounding medium.

As an exapmle let us consider the gas contained in a vertical cylinder fitted with a piston. To create a reversible process of compression occurring during an infinitely long time, the load onto the piston must be increased by infinitely small amounts. But if a working medium realizes a process with finite velocities, or rates, such a process shall be irreversible. At a finite piston velocity the gas located immediately in the vicinity of the piston shall exert a pressure greater than the gas in the remaining volume, and it will take some time for the pressure to even out over the entire volume.

Upon expansion of the gas the phenomena shall be observed in a reverse sequence. The pressure of the gas directly near the piston shall be lower than in the remaining volume, and it will take some time for the gas to expand and occupy the entire volume of the cylinder. Thus, *processes* of expansion and compression proceeding with *finite velocities*, or rates, are *irreversible thermodynamic processes.*

The finite rate at which an irreversible process develops is always associated with an additional expenditure of energy to overcome the frictional forces. Since a reverse non-compensated conversion of heat into work is impossible, any process accompanied by friction is an irreversible one. Also irreversible are processes occurring at finite differences between the temperature of the working medium and that of the source of heat, processes of diffusion, process of expansion in a vacuum, and others.

Reversible thermodynamic processes are ideal processes in which an expanding gas produces maximum work, determined by equation

$$l = \int_{v_1}^{v_2} p\, dv,$$

where p is the pressure of the working medium, equal to that of the surrounding medium.

In a process of compression, when the working medium returns to its initial state, minimum work is expended in a reversible process.

The work performed by a gas in irreversible processes is determined by the following equation

$$l = \int_{v_1}^{v_2} p'\, dv,$$

where p' is the pressure of the surrounding medium.

When a gas expands l_{rev} is always greater than l_{ir}, $l_{rev} > l_{ir}$, and when a gas is compressed, on the contrary, $l_{rev} < l_{ir}$.

Only reversible processes can be shown graphically on *p-v* and *T-v* diagrams, since on these diagrams each point represents an equilibrium state of the body involved, whereas it is either impossible to represent irreversible processes on *p-v* and *T-v* diagrams, or an approximate graphical presentation of them can be made, replacing, for instance, all properties with volume-averaged values.

Thermodynamics studies reversible processes taking place in idealized systems at infinitely low velocities or rates. Under these conditions any process can be subjected to a comprehensive thermodynamic and mathematical analysis, if the properties of the working medium are known.

All real processes taking place in nature and in engineering applications are accompanied by the phenomena of friction or heat conduction at finite temperature differences and they are, therefore, irreversible. However, many of the irreversible processes dealt with in practice, differ comparatively little from reversible processes. In practical calculations engineers pass from reversible processes to real ones with the aid of empirical coefficients accounting for the deviation of the real processes from ideal, reversible, processes.

Thus, a reversible process is some extreme, or limiting, case of a real process.

5-5. Mathematical Statement of the First Law of Thermodynamics

Let 1 kg of gas undergo some process (Fig. 5-10) on the elementary section of which, *a-b*, an infinitely small amount of energy is added in the form of heat *dq* with the temperature and volume of the working medium increasing correspondingly by infinitely small values *dT* and *dv*.

As the temperature of the working medium increases by *dT*, molecular velocity rises or its internal kinetic energy increases. When the volume of the working medium increases by *dv*, the distance between molecules increases, which is associated with an increase in the internal potential energy of the medium.

The sum of the changes in the internal kinetic and internal potential energies represents the full change in internal energy *du*.

As the volume increases by *dv*, the working medium performs work on the surrounding medium (or external work) to overcome external forces, which is denoted by *dl*.

If no other phenomena of any kind proceed in the working medium and there is no kinetic energy of apparent mo-

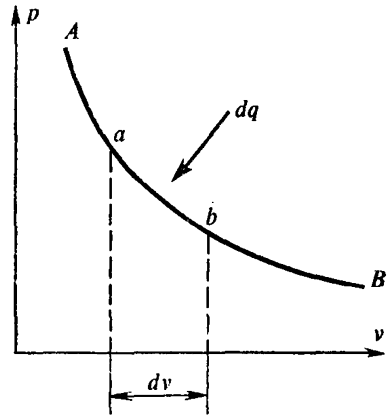


FIG. 5-10

tion, then in accordance with the law of conservation of energy and with account taken of the selected rule of signs, we can write for an elementary process the following equation

$$du=dq-dl; \quad u_2-u_1=\int_1^2 dq-\int_1^2 dl=q_{1\text{-}2}-l_{1\text{-}2} \tag{5-8}$$

or for reversible processes

$$dq=du+p\,dv; \quad q_{1\text{-}2}=u_2-u_1+\int_1^2 p\,dv \tag{5-9}$$

The obtained expression is the mathematical statement of the first law of thermodynamics. The law is formulated as follows: *a change in the internal energy of a thermodynamic system is equal to the algebraic sum of the energy transferred to it in the form of heat dq and the work dl done by that heat against external forces, or the energy added to a working medium in the form of heat is expended in changing its internal energy and in the work done by the medium to overcome external forces (work done on surroundings).*

The main mathematical statement of the first law of thermodynamics (5-8 and 5-9) as the law of conservation of energy was obtained for processes in which the only kind of work was that of expansion, $p\,dv$, but strictly speaking it is valid for any systems, both stationary and those in motion (flow processes).

For flow processes the mathematical statement of the first law of thermodynamics is a special case of the two general equations (5-8) and (5-9).

Let us consider the mathematical statement of the first law of thermodynamics as applied to a flow process.

As a gas flows through any section of a channel *1-2* (Fig. 5-11) the work being spent to displace 1 kg of gas from the apparatus is equal to $p_2 f_2 s_2$ or $p_2 v_2$. This work is done by the flow against external forces and is considered to be positive.

The work done on the flow in section *1*, spent to force 1 kg of the gas to flow into the channel is equal to $p_1 f_1 s_1$ or $p_1 v_1$. This work is considered to be negative. Thus, the work done in section *1-2* of the channel is equal to the algebraic sum of works $p_2 v_2$ and $p_1 v_1$, referred to as displacement work $l'=p_2 v_2-p_1 v_1$ or $dl'=d(pv)$.

If the kinetic energy of the working medium in section *2* (with a flow velocity w_2) is greater than the kinetic energy of the medium in section *1* (with a flow velocity w_1), then the change in the kinetic energy of flow is determined from the relationship, known from mechanics,

$$l_{kin}=w_2^2/2-w_1^2/2 \quad \text{or} \quad dl_{kin}=dw^2/2.$$

This increase in the kinetic energy of flow is called the *available work* and can be used to rotate the shaft of a machine.

If the sections *1* and *2* are located on different heights, then work must be spent to elevate the working medium from the height h_1 to the height h, or work must be spent to change the external potential energy of flow, amounting to $l_{pot}=h-h_1$, or $dl_{pot}=dh$.

In the general case the flow between the sections *1* and *2* of the channel can perform different kinds of useful work in steam and gas turbines, compressors, fans, induced-draft fans, etc. All these kinds of work are referred to as *mechanical*, or *shaft, work* and are denoted by l_{mech} or dl_{mech}.

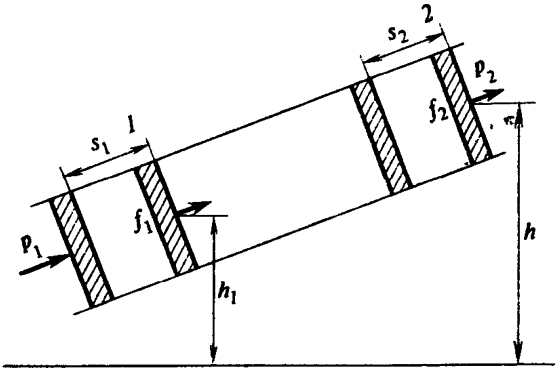


FIG. 5-11

As a gas passes through a channel, work is being spent to overcome skin friction. This work is denoted by l_{fr} or dl_{fr}.

Thus, the work done by the flow of a working medium can be presented in the following form

$$l_{1\text{-}2}=(p_2v_2-p_1v_1)+(w_2^2/2-w_1^2/2)+(h-h_1)+l_{mech}+l_{fr},$$

or

$$dl_{1\text{-}2}=d(pv)+dw^2/2+dh+dl_{mech}+dl_{fr}.$$

Substituting the obtained expression of work into Eq. (5-8) expressing the first law of thermodynamics, we get

$$q_{1\text{-}2}=(u_2-u_1)+(p_2v_2-p_1v_1)+(w_2^2/2-w_1^2/2)+(h-h_1)+l_{mech}+l_{fr}, \qquad (5\text{-}10)$$

or in the differential form

$$dq=du+d(pv)+dw^2/2+dh+dl_{mech}+dl_{fr}.$$

The derived equation of the first law of thermodynamics is valid for any working media and, in particular, for ideal gases. These equations (5-8) through (5-10) describe both reversible and irreversible processes.

In fact, in irreversible processes the work l_{fr}, expended to overcome

friction forces, fully converts into frictional heat, therefore $q_{fr}=l_{fr}$ or $dq_{fr}=dl_{fr}$. Then, for irreversible processes

$$dq+dq_{fr}=du+d(pv)+dw^2/2+dh+dl_{mech}+dl_{fr}.$$

But in this equation dq_{fr} and dl_{fr} cancel mutually and the mathematical statement of the first law of thermodynamics takes the form

$$dq=du+d(pv)+dw^2/2+dh+dl_{mech}, \tag{5-11}$$

whence it follows that equations (5-8) and (5-11) also describe irreversible processes.

Thus, equations (5-9) and (5-11) express the first law of thermodynamics, and the amount of work $p\,dv$ can be equated to the right-hand side of Eq. (5-11), $p\,dv=d(pv)+dw^2/2+dh+dl_{mech}$. It follows from this equation that all kinds of flow work are done at the expense of the work $p\,dv$ due to expansion of the working medium.

All quantities in Eq. (5-8) can be both positive and negative and become equal to zero in some cases.

Notwithstanding its simplicity there are a great number of statements of the first law of thermodynamics.

Let us give the most widespread statements.

1. *Energy cannot be created nor can it be destroyed.* This statement tells us that energy cannot appear from nothing, nor can it convert into nothing.

2. *Any form of motion is able of and must convert into any other form of motion.* This philosophic statement proposed by F. Engels underlines the fact that energy does not vanish and its ability to convert into any other form of energy.

3. *Perpetual motion of the first kind is impossible.* By perpetual motion of the first kind is meant a machine that would be able to produce work out of nothing.

4. *Energy is a single-valued function of state.* For instance, the internal energy is a single-valued, or unambiguous, function of the main parameters of state, $u=f(p, v, T)$.

5. *An infinitely small change in internal energy is a total differential.* This mathematical statement underlines that if u is energy, then du must be its total differential.

6. *Heat and work are the only two possible forms of energy transfer from one body to another.* The two concepts of heat and work are associated not with a "store", but with a "process". Work is the macrophysical form of energy transfer, and heat represents the totality of the macrophysical processes of energy transfer.

5-6. Enthalpy

In the last century the famous physicist J. Gibbs introduced a new function to be used in practical calculations, and this function, as suggested by Kamerlingh Onnes, was given the name of *enthalpy*. Specific enthalpy,

i.e. enthalpy reduced to 1 kg, is denoted by the letter i and measured in joules per kilogram (J/kg); hence, by definition, it is a complex function of the kind

$$i=u+pv. \tag{5-12}$$

Inasmuch as the quantities u, p and v, defining enthalpy, are functions of state, hence, enthalpy is also a function (or property) of state.

Enthalpy is an additive or extensive parameter, since its magnitude is proportional to mass.

If pressure p and temperature T are chosen as independent parameters, it is possible to obtain for reversible processes another mathematical statement of the first law of thermodynamics

$$dq=du+p\,dv=du+d(pv)-v\,dp=d(u+pv)-v\,dp.$$

Whence

$$dq=di-v\,dp, \tag{5-13}$$

or

$$q_{1\text{-}2}=i_2-i_1-\int_{p_1}^{p_2} v\,dp. \tag{5-14}$$

The absolute value of the enthalpy of a thermodynamic system can be obtained by integrating Eq. (5-13). Upon integration the integration constant i_0 shall be present in the expression for i

$$i=\int (dq+v\,dp)+i_0, \tag{5-15}$$

i.e. the enthalpy of a system is determined with precision limited by some additive constant i_0. This constant is selected arbitrarily and usually the enthalpy of an ideal gas (at $p\to 0$) is assumed to be equal to zero at 0 °C, and the integration constant is ignored.

If reversible processes occur in a thermodynamic system and along with the work involved in a change in volume, pdv, work is produced that is not associated with the change in system volume and can be transferred to an external object, there will appear an additional term l_v in the hand-right sides of Eqs. (5-10) and (5-13)

$$dq=du+p\,dv+dl_v; \tag{5-16}$$

$$dq=di-v\,dp+dl_v. \tag{5-17}$$

Equations (5-16) and (5-17) are the most general mathematical statement of the first law of thermodynamics for reversible processes in which a thermodynamic system undergoes a change of state.

At $p=\text{const}$ Eq. (5-13) turns into

$$dq_p=di. \tag{5-18}$$

The differential of enthalpy *di* is the elementary amount of heat involved in a constant-pressure process. All the heat involved in the process taking place at constant pressure is expended to change the enthalpy

$$q_p = \int_1^2 di = i_2 - i_1. \tag{5-19}$$

It follows from Eq. (5-13) that

$$di = dq + v\,dp, \quad \text{or} \quad i_2 - i_1 = q + \int_{p_1}^{p_2} v\,dp. \tag{5-20}$$

Enthalpy is greater than the external heat by the amount of work $v\,dp$ which is represented on a *p-v* diagram by the elementary area *abcd*, as illustrated in Fig. 5-12.

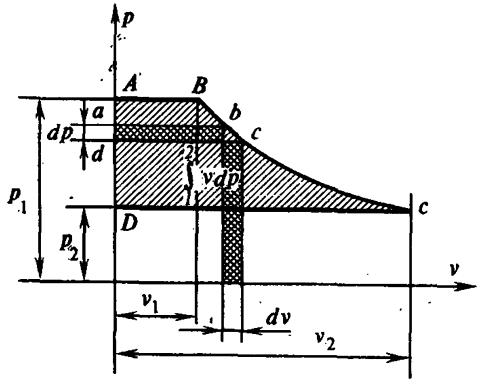


FIG. 5-12

A change in enthalpy is fully determined by the initial and final states of a working medium and is independent of the intermediate states. In a cyclic process the change in enthalpy is zero, i.e.

$$\oint di = 0.$$

Inasmuch as enthalpy is a function of the main parameters of state, *di* is the total differential of this function for any independent variables characterizing the state of a gas

$$i = f(p, v); \quad i = \varphi(v, T); \quad i = F(p, T),$$

whence

$$\left.\begin{aligned} di &= (\partial i/\partial p)_v\,dp + (\partial i/\partial v)_p\,dv, \\ di &= (\partial i/\partial T)_v\,dT + (\partial i/\partial v)_T\,dv, \\ di &= (\partial i/\partial T)_p\,dT + (\partial i/\partial p)_T\,dp. \end{aligned}\right\} \tag{5-21}$$

The change in enthalpy in all processes occurring between two points *A* and *B* is the same (Fig. 5-13). The physical meaning of enthalpy will be clear by considering the following example. A piston moving in a cylinder filled with 1 kg of gas carries a load of *m* kg (Fig. 5-14). The area of the piston is *f*, the internal energy of the working medium—*u*. The potential

energy of the load is equal to the product of its mass m by the height S. Since the pressure of the gas p is balanced by the mass of the load, then the potential energy of the mass can be expressed as

$$mS=pfS.$$

The product fS is the specific volume of the gas. Whence

$$mS=pv.$$

The product of pressure by volume is the work that must be expended to force a gas of volume v into an external surrounding medium at a pressure p. Thus, the work pv is the potential energy of the gas, depending on the forces acting upon the piston. The greater the external forces, the higher the pressure p, and the greater the potential energy of the gas pv.

If the gas, filling the cylinder, and the piston with the load are considered as composing a single system, which shall be referred to as an *expanded system*, the total energy E of this system is the sum of the internal energy of the gas u and potential energy of the piston with the load, equal to pv

$$E=u+pv=i. \qquad (5\text{-}22)$$

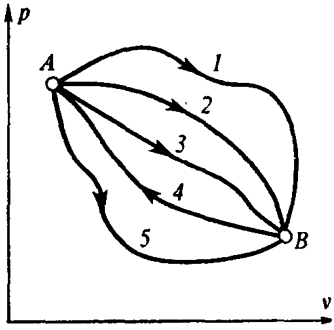


FIG. 5-13

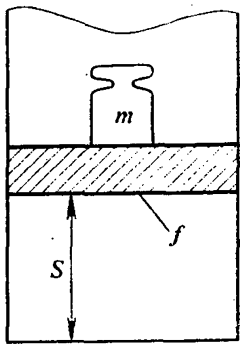


FIG. 5-14

It follows from this that enthalpy i is equal to the energy of the expanded system composed of the working medium and surroundings. This is the physical meaning of enthalpy.

The values of enthalpy for vapours, gases, and mixtures of gases are given in technical literature and in handbooks. Making use of these data, it is possible to determine the amount of heat participating in a process at constant pressure. Enthalpy is of great importance and finds wide application in calculations for heat and refrigerating installations and it considerably simplifies calculations when used as a parameter of state of the working medium. Enthalpy permits to use graphical investigation of various thermodynamic processes and cycles.

It is especially expedient to use enthalpy when p and T are used as the main parameters. This can be clearly visualized, if enthalpy i is compared with internal energy u. With $v=\text{const}$ the equation of the first law of thermodynamics, $dq=du+p\,dv$, turns into the equation $dq_v=du$, or $q_v=u_2-u_1$, and with $p=\text{const}$, $q_p=i_2-i_1$.

Just as internal energy, the enthalpy of an ideal gas is a function of

temperature and is independent of other parameters of state. In fact, for an ideal gas

$$i=u(T)+pv=u(T)+RT,$$

hence (inasmuch as both items depend only on temperature), $i=f(T)$.

Then, by analogy with internal energy we have

$$(\partial i/\partial T)_p=(\partial i/\partial T)_v=di/dT, \tag{5-23}$$

i.e. in any process in which an ideal gas undergoes a change of state the derivative of the change in enthalpy with respect to temperature shall always be a total derivative.

The numerical values of the enthalpy of ideal gases are given in Table XIII, in the Appendix.

Typical Questions and Examples to Chapter Five

1. What is meant by the internal energy of an ideal gas and of a real gas?
2. On what parameters of state does the internal energy of an ideal and real gases depend?
3. Is the internal energy a function of state or of a process?
4. What is the change of the internal energy in a cyclic process equal to?
5. Derive the equation of work done in an arbitrary process.
6. What does the area under the curve of a process plotted on a p-v diagram represent?
7. Prove that work is a function of a process.
8. Give the definitions of a reversible and irreversible process.
9. What are the characteristics of reversible processes?
10. When does a gas produce more work: in a reversible or irreversible process?
11. Is it possible to give a graphical representation of a reversible and irreversible process?
12. Is it possible to realize practically a reversible process?
13. What is the statement of the first law of thermodynamics?
14. What is the mathematical statement of the first law of thermodynamics?
15. What is meant by enthalpy?
16. What is the other mathematical statement of the first law of thermodynamics (with the use of enthalpy)?
17. What is the physical meaning of enthalpy?

Example 5-1. Determine the hourly consumption of fuel required to operate a steam turbine rated at 500 kW, if the heating value of fuel is 30 000 kJ/kg and the efficiency of the power plant amounts to 20 per cent.

$$m=\frac{500\times 60\times 60}{30\,000\times 0.2}=300 \text{ kg}.$$

Example 5-2. At an initial temperature of 30 °C, 10 kg of air undergoes a change in state to a final temperature of 300 °C. Determine the change in the internal energy of the air, assuming it to be an ideal gas.

From Table XIII in the Appendix we find that the change in internal energy

$$m(u_2-u_1)=10(219.5-21.5)=1980 \text{ kJ}.$$

Example 5-3. In the boiler house of an electric power plant 100 t of coal is fired during 10 hours of operation. The heating value of the coal is 28 000 kJ/kg. Determine the amount of electric power generated and the rating of the electric power plant, if plant efficiency is 20 per cent.

The capacity of the electric power plant

$$N=\frac{100\times1000\times28\,000\times0.2}{10\times3600}=15\,555 \text{ kW}.$$

The amount of electric power generated is

$$W=\frac{100\times1000\times28\,000\times0.2}{3600}=155\,555 \text{ kW}\cdot\text{h}=560 \text{ GJ}.$$

CHAPTER SIX

HEAT CAPACITY OF GASES. ENTROPY

6-1. Basic Definitions

In calculating various heat apparatus, it is of paramount importance to determine the amount of heat involved in the process. An exact determination of the amount of heat ensures correct evaluation of the efficient performance of the apparatus especially when conducting comparative tests.

The addition of heat to a body in any process causes a change in its state and is accompanied, in the general case, by a change in temperature. The ratio of the heat dq transferred to unit substance, causing an infinitely small change in its state, to the change in temperature dt is called the *specific heat capacity* of the body involved in the given process

$$c_x = \frac{dq_x}{dt}. \tag{6-1}$$

The quantity q in Eq. (6-1) depends not only on the temperature interval, but also on the kind of the heat-transfer process, characterized by some constant parameter x, which may be the volume of the body v, pressure p, etc. The total amount of heat transferred in the given process is determined by the expression

$$q_{1\text{-}2,x} = \int_{t_1}^{t_2} c_x \, dT, \tag{6-2}$$

where the integral is taken from the initial state *1* to the given final state *2*.

Unasmuch as the quantity of heat $dq_{1\text{-}2,x}$ depends on the nature of the process, the heat capacity c_x of the system also depends on the conditions under which the process takes place. Depending on the nature of the process, one and the same system possesses different heat capacities, the numerical value of which may vary form $-\infty$ to $+\infty$.

6-2. Mass, Volume and Molar Heat Capacities of Gases

The mass, volume and molar heat capacities are distinguishable in thermodynamics.

Heat capacity reduced to 1 kg of gas is referred to as the *mass heat capacity* and is denoted by c_x. This heat capacity is measured in units of kJ/kg·deg.

Heat capacity reduced to 1 m³ of gas in standard physical conditions, i.e. at a pressure of 101 325 N/m² and a temperature of 0 °C, is called the *volume heat capacity* and is denoted by c'_x. It is measured in units of kJ/m³·deg.

Heat capacity reduced to 1 kmole of gas is referred to as the *molar heat capacity*, denoted by μc_x and measured in units of kJ/kmole·deg.

The mass, volume and molar heat capacities are interrelated as follows

$$c_x = c'_x v_0 = \mu c_x / \mu,$$

where v_0 = specific volume under standard thermodynamic conditions;
μ = molecular mass.

6-3. Analytical Expressions for Heat Capacities c_v and c_p

As was pointed out above, heat capacities depend on the nature of the process. Of great importance in thermodynamics is the constant-volume, or isochoric, heat capacity

$$c_v = \frac{dq_v}{dT}, \tag{6-3}$$

equal to the ratio of the amount of heat dq_v in a process occurring at constant volume to the change in body temperature dT, and constant-pressure, or isobaric, heat capacity

$$c_p = \frac{dq_p}{dT}, \tag{6-4}$$

equal to the ratio of the amount of heat dq_p in a process occurring at constant pressure to the change in body temperature dT.

In a process of equilibrium heating the elementary amount of heat involved is determined by Eq. (5-9)

$$dq = du + p\,dv,$$

and, since it follows from Eq. (5-3) that

$$du = (\partial u/\partial v)_T\,dv + (\partial u/\partial T)_v\,dT,$$

then

$$dq = (\partial u/\partial T)_v\,dT + [(\partial u/\partial v)_T + p]\,dv. \tag{6-4'}$$

For a constant-volume, or isochoric, process Eq. (6-4') acquires the following appearance

$$dq_v = (\partial u/\partial T)_v\,dT.$$

Therefore, with v=const the expression for heat capacity can be presented in the following form

$$c_v = (\partial u/\partial T)_v, \tag{6-5}$$

i.e. at $v=\text{const}$ heat capacity c_v is the partial derivative of internal energy u (considered as a function of T and v) with respect to temperature T.

In addition, it follows from Eqs. (6-3) and (6-5) that in a process proceeding at $v=\text{const}$ in which the body performs no external work all the heat transferred to the body is expended to change its internal energy

$$dq_v=du_v=c_v\,dT_v, \tag{6-6}$$

or at $c_v=\text{const}$

$$q_{1\text{-}2,\,v}=u_2-u_1=c_v(t_2-t_1).$$

The change in the internal energy of an ideal gas is equal to the product of the constant-volume heat capacity by the difference between the temperatures of the body in any process.

In fact, for an ideal gas, whose internal energy is only a function of temperature, the partial derivative $\left(\frac{\partial u}{\partial v}\right)_T$ will be equal to zero. Then, $du=(\partial u/\partial T)_v\,dT$, or $du=c_v\,dT$, irrespective of the nature of the process.

Integrating Eq. (6-6) for an ideal gas between the limits from 0 °C to t, we obtain

$$u=\int_0^t c_v\,dt=c_{vm}\Big|_0^t t,$$

where $c_{vm}=$mean heat capacity at $v=\text{const}$.

It follows from the foregoing that for any finite process of a change in state of an ideal gas we have

$$u_2-u_1=c_{vm}\Big|_{t_1}^{t_2}(t_2-t_1)=c_{vm}\Big|_0^{t_2}t_2-c_{vm}\Big|_0^{t_1}t_1.$$

Substituting the value $du=c_v\,dT$ into the main mathematical statement (equation) of the first law of thermodynamics (5-9), in the general case we have for a reversible process occurring with an infinitely small change in the state of an ideal gas

$$dq=c_v\,dT+p\,dv. \tag{6-7}$$

Using T and v as independent variables, the equation of the first law of thermodynamics yields

$$dq=(\partial u/\partial T)_v\,dT+[p+(\partial u/\partial v)_T]\,dv, \tag{6-7'}$$

whence, at $p=\text{const}$

$$dq_p=(\partial u/\partial T)_v\,dT_p+[p+(\partial u/\partial v)_T]\,dv_p$$

or, inasmuch as $dq_p=c_p\,dT_p$,

$$c_p=(\partial u/\partial T)_v+[p+(\partial u/\partial v)_T](\partial v/\partial T)_p. \tag{6-8}$$

Applying Eq. (6-5), we obtain

$$c_p = c_v + [p + (\partial u/\partial v)_T](\partial v/\partial T)_p. \tag{6-9}$$

Equation (6-9) relates in a general way the heat capacities c_p and c_v.

Since $(\partial u/\partial v)_T = 0$, and it follows from the equation of state $pv = RT$ that $p(\partial v/\partial T)_p = R$, for an ideal gas,

$$c_p = c_v + R \quad \text{and} \quad c_p - c_v = R. \tag{6-10}$$

This equation is known as *Mayer's relation*. It can also be written for 1 kmole of gas

$$\mu c_p = \mu c_v + \mu R, \quad \text{or} \quad \mu c_p - \mu c_v = 8.3142 \text{ kJ/kmole·deg}.$$

Thus, for an ideal gas the difference between μc_p and μc_v is constant.

The expression for heat capacity c_p can also be derived, using pressure p and temperature T as independent parameters. Then, in accordance with Eq. (5-13)

$$dq = di - v\,dp$$

or

$$dq = (\partial i/\partial T)_p\,dT - [v - (\partial i/\partial p)_T]\,dp, \tag{6-11}$$

whence it follows that at $p = \text{const}$

$$dq_p = (\partial i/\partial T)_p\,dT_p$$

and, consequently, constant-pressure heat capacity

$$c_p = (\partial i/\partial T)_p, \tag{6-12}$$

i.e. at $p = \text{const}$ the heat capacity of a body c_p is equal to the partial derivative of enthalpy i with respect to temperature T and is a function of p and T.

Inasmuch as the enthalpy of an ideal gas is independent of pressure and volume and is only a function of temperature, it can easily be shown that for any process the heat capacity c_p of an ideal gas is equal to

$$c_p = di/dT.$$

Then, for an ideal gas the mathematical statement of the first law of thermodynamics

$$dq = di - v\,dp$$

can be presented in the following form

$$dq = c_p\,dT - v\,dp. \tag{6-13}$$

With independent variables v and T the first law of thermodynamics takes another appearance

$$dq = c_v\,dT + p\,dv,$$

but

$$p=RT/v=T(\partial p/\partial T)_v, \quad \text{where} \quad R/v=(\partial p/\partial T)_v$$

and

$$dq=c_v\,dT+T(\partial p/\partial T)_v\,dv. \tag{6-14}$$

Equation (6-14) can be used to relate the heat capacities c_p and c_v. For an isobaric (constant-pressure) process Eq. (6-14) takes the appearance

$$dq_p=c_v\,dT_p+T(\partial p/\partial T)_v\,dv_p. \tag{6-15}$$

Dividing the left- and right-hand sides of Eq. (6-15) by dT_p

$$dq_p/dT_p=c_v\,dT_p/dT_p+T(\partial p/\partial T)_v\,dv_p/dT_p,$$

and taking into account that $dq_p=c_p\,dT_p$, we obtain

$$c_p-c_v=T(\partial p/\partial T)_v(\partial v/\partial T)_p. \tag{6-16}$$

If the equation of state of a real gas is known, and also the heat capacity c_p that can be determined by experiment, then Eq. (6-16) can be used to determine c_v whose determination by experiment involves great difficulties. It should be noted that for real gases

$$c_p-c_v>R.$$

This inequality can be explained by the fact that upon expansion (at $p=\text{const}$) real gases perform not only external, but also internal work associated with the change in potential energy of the body and it is exactly this that causes a high rate of heat transfer.

6-4. Elements of the Molecular-Kinetic and Quantum Theory of Heat Capacity

The classical molecular-kinetic theory of gases considers an ideal gas as the totality of absolutely rigid molecules between which no forces of interaction exist and each molecule possesses but energy due to translational and rotational motion, and the molecules proper are considered to be material points.

The translational motion of such a molecule can be decomposed in the directions of three coordinate axes and, accordingly, a molecule is said to possess three degrees of freedom of translational motion. The number of rotational degrees of freedom shall depend on the atomicity, or valency, of the gas.

In accordance with the kinetic energy, the internal energy of gases is distributed uniformly in respect to the degrees of freedom of translational and rotational molecular motion.

A monoatomic gas has three degrees of freedom of translational motion ($i=3$). In addition to rotational motion, the molecule of a diatomic gas can also be in rotational motion about a common centre of gravity, arranged on the line connecting both atoms. Such a molecule of a diatomic gas has

five degrees of freedom ($i=5$) of which: three degrees of freedom of translational motion and two degrees of freedom of rotational motion.

The molecules of triatomic and polyatomic gases have three degrees of freedom of translational motion and three degrees of freedom of rotational motion, with the total number of degrees of freedom $i=6$.

In order to calculate the fraction of the internal energy per one degree of freedom, let us consider an ideal monoatomic gas possessing only three degrees of freedom of translational motion.

It is known from the kinetic theory that the pressure exerted by an ideal gas on the walls of the confining vessel is equal to 2/3 of the mean kinetic energy of translational motion of atoms, i.e.

$$p=(2/3)nm\bar{w}^2/2, \tag{6-17}$$

where p = gas pressure, N/m^2;
n = number of atoms in 1 m^3 of gas;
m = mass of one atom;
$\bar{w}$ = root-mean-square atomic velocity determined from equation

$$\bar{w}^2=(w_1^2+w_2^2+w_3^2+\ldots+w_n^2)/n,$$

where w_1, w_2, ..., w_n are the velocities of individual atoms.

Multiplying both sides of Eq. (6-17) by the volume of a kilomole, V_μ, we obtain the equation for 1 kmole

$$pV_\mu=(2/3)nV_\mu m\bar{w}_2/2.$$

In the above equation the product $nV_\mu=N$ is the number of atoms in 1 kmole of gas (Avogadro's number):

$$pV_\mu=(2/3)Nm\bar{w}^2/2.$$

The quantity $m\bar{w}^2/2$ is the mean kinetic energy of the translational motion of a single atom of gas, and since the total number of atoms is N, the total kinetic energy of 1 kmole of a monoatomic gas, equal to the kinetic energy of all atoms, amounts to

$$\mu u=Nm\bar{w}^2/2.$$

Then

$$pV_\mu=(2/3)_{\mu u} \quad \text{or} \quad \mu u=(3/2)pV_\mu. \tag{6-18}$$

Substituting pV_μ with its value from the equation of state, we find that

$$\mu u=(3/2)\mu RT, \tag{6-19}$$

and since $\mu R=8.3142$ kJ/kmole·deg, then for a monoatomic gas

$$\mu u=(3/2)\times 8.3142T=12.5T. \tag{6-20}$$

Taking from Eq. (6-19) the derivative of internal energy with respect to temperature, we obtain

$$d\mu u/dT=\mu c_v=(3/2)\mu R. \tag{6-21}$$

It is obvious from the equation that μc_v does not depend on temperature. It follows that Eq. (6-19) expresses the internal energy of a monoatomic ideal gas obeying the equation $pV_\mu = \mu RT$ and for which $\mu c_v = \text{const}$.

The numerical value of the molar heat capacity for a monoatomic gas is equal to

$$\mu c_v = (3/2)\mu R = 12.5 \text{ kJ/kmole·deg}.$$

It follows from the foregoing that in a monoatomic gas energy amounting to 12.5:3=4.16 kJ/kmole·deg is spent for each degree of freedom. Substituting the value of the heat capacity μc_v from Eq. (6-21) into Mayer's relation, we find that

$$\mu c_p = [(i+2)/2]\mu R, \tag{6-22}$$

or for a monoatomic gas

$$\mu c_p = [(3+2)/2]8.3142 \approx 20.8 \text{ kJ/kmole·deg}.$$

Experimental studies conducted with monoatomic gases substantiated the data obtained analitically.

Assuming that in a diatomic gas the amount of energy spent for each degree of freedom is equal to that expended for one degree of freedom of translational motion in a monoatomic gas, we find that for a diatomic gas

$$\mu c_v = 4.16 \times 5 \approx 20.8 \text{ kJ/kmole·deg},$$

$$\mu c_p = [(5+2)/2]8.3142 \approx 29.1 \text{ kJ/kmole·deg}.$$

For comparatively high temperatures, however, there is a considerable discrepancy between the above indicated values of the heat capacities of diatomic gases and experimental data. The discrepancy is still greater for triatomic and polyatomic gases.

This discrepancy is traced to the fact that when considering complex molecules not only translational and rotational motion must be taken into account, but also an allowance should be made for the oscillatory motion of the atoms in the molecule itself, whose energy is ignored in the kinetic theory of gases.

The energy of the oscillatory motion of atoms in a molecule is taken into account in the quantum theory of heat capacities. This theory proves that the heat capacity of diatomic and polyatomic gases is a function of temperature, since the energy of oscillatory motion of atoms in a molecule does not vary in direct proportion to temperature.

Making use of Planck's quantum theory, A. Einstein obtained the following expression for the molar heat capacity which is sufficiently accurate for the temperatures used in heat engineering

$$\mu c_v = i_1 \mu R/2 + \sum_1^{i_2} \mu R \left(\frac{\theta}{T}\right)^2 [e^{\theta/T}/(e^{\theta/T}-1)^2], \tag{6-23}$$

where i_1 = the number of degrees of freedom of translational and rotational molecular motion;

i_2 = number of degrees of freedom of intermolecular oscillation;
θ = characteristic temperature of oscillatory motion, equal to $\theta = h\omega/k$ (h = Planck's constant, k = Boltzmann constant, ω = number of oscillations per second);
e = base of natural logarithms;
T = absolute gas temperature.

In the right-hand side of formula (6-23) the first term takes into account the amount of energy expended in varying the translational and rotational motion of molecules; it is determined by the number of degrees of freedom associated with these motions. The second term in the formula accounts for the energy spent to change the intramolecular oscillations; it is determined by the number of oscillatory degrees of freedom.

Formula (6-23) is not absolutely correct, since certain assumptions were made in deriving it.

For approximate calculations of processes taking place at not very high temperatures, it is advisable to make use of the constant molar heat capacities μc_v and μc_p derived with a certain correction for triatomic and polyatomic gases, based on the molecular-kinetic theory of heat capacity. These data are given in Table 6-1.

TABLE 6-1

Gas atomicity	μc_v, kJ/kmole·deg	μc_p, kJ/kmole·deg
Monoatomic gas	12.5	20.8
Diatomic gas	20.8	29.1
Tri- and polyatomic gases	29.1	37.4

The exact values of the heat capacities of ideal gases depending on temperature are given in special tables, and they are calculated on the basis of spectroscopic data and the method of quantum statistics.

6-5. True and Average Heat Capacities

Since the heat capacity of an ideal gas depends on temperature and that of a real gas also on pressure, in addition to temperature, in engineering thermodynamics the true and average heat capacities are distinguished.

The heat capacity, determined by Eqs. (6-1), (6-3), (6-4) at given properties of state v and T or p and T (i.e. in a given state), is referred to as the true heat capacity. Hence, by the *true heat capacity* is meant *the ratio of the elementary amount of heat transferred to a thermodynamic system undergoing any process to an infinitely small temperature difference.*

The true heat capacities of ideal gases can be expressed as the sum of two terms

$$c_x = c_{x0} + \Delta c_x.$$

The first item is the heat capacity of the given gas in a rarefied (ideal) state (at $p \to 0$ or $v \to \infty$) and it depends only on temperature.

With respect to temperature the heat capacities c_p and c_v can be approximately related by the following polynomial of third order

$$c_{x0} = a_0 + a_1 t + a_2 t^2 + a_3 t^3.$$

However, at present, more exact table data are used in calculations.

The second item Δc_x determines the dependence of heat capacity on pressure or specific volume and is associated with a change in the potential component of the internal energy of a real gas.

In practical calculations, when determining the amounts of heat, use is generally made of the so-called average heat capacities.

By the average heat capacity c_{xm} of a given process, occurring in a temperature interval from t_1 to t_2, is meant the *ratio of the amount of heat* q_{1-2} to the finite temperature difference $t_2 - t_1$:

$$c_{xm}\Big|_{t_1}^{t_2} = \frac{q_{1-2,x}}{t_2 - t_1} \tag{6-24}$$

Since the quantity of heat $q_{1-2,x}$ transferred to a system undergoing a process at $x = \text{const}$ is determined by Eq. (6-2), where c_x is the true heat capacity for the given process, then

$$c_{xm}\Big|_{t_1}^{t_2} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} c_x \, dt. \tag{6-25}$$

Equation (6-25) relates the average and true heat capacities of the body involved in a given process.

If the average heat capacities are tabulated for a temperature interval from 0° to t °C, the average heat capacity $c_{xm}\Big|_{t_1}^{t_2}$ can be calculated by formula (see Fig. 6-1)

$$c_{xm}\Big|_{t_1}^{t_2} = \frac{c_{xm}\Big|_0^{t_2} t_2 - c_{xm}\Big|_0^{t_1} t_1}{t_2 - t_1}. \tag{6-26}$$

In fact, as is generally known from integral calculus the integral in Eq. (6-25) can be integrated by parts as follows

$$c_{xm}\Big|_{t_1}^{t_2} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} c_x \, dt = \frac{1}{t_2 - t_1} \left[\int_0^{t_2} c_x \, dt - \int_0^{t_1} c_x \, dt \right],$$

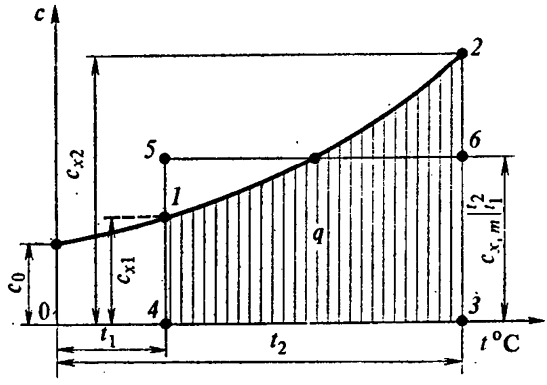


FIG. 6-1

but

$$\int_0^{t_2} c_x\,dt = c_{xm}\Big|_{t_0}^{t_2} t_2, \quad \text{and} \quad \int_0^{t_1} c_x\,dt = c_{xm}\Big|_{t_0}^{t_1} t_1.$$

Substituting the found values of the integrals into Eq. (6-25), we obtain Eq. (6-26).

Thus, if in some kind of a process an ideal gas was heated from a temperature t_1 to t_2, then the quantity of heat expended in the heating is equal to

$$Q_x = m\left[c_{xm}\Big|_0^{t_2} t_2 - c_{xm}\Big|_0^{t_1} t_1\right] = V_h\left[c'_{xm}\Big|_0^{t_2} t_2 - c'_{xm}\Big|_0^{t_1} t_1\right]. \tag{6-27}$$

The average molar, mass and volume heat capacities of gases at $p=\text{const}$ and $v=\text{const}$ are given in Tables III-VIII of the Appendix.

6-6. Ratio of Heat Capacities c_p and c_v

In thermodynamics use is often made of the ratio of the heat capacity at a constant pressure to the heat capacity at a constant volume, denoted by the letter k

$$k = c_p/c_v = c'_p/c'_v = \mu c_p/\mu c_v.$$

According to the classical kinetic theory of gases the quantity k is determined by the number of freedom of molecular motion. It follows from Eqs. (6-21) and (6-22) that

$$k = \frac{i+2}{2}R; \quad \frac{i}{2}R = 1 + \frac{2}{i}. \tag{6-28}$$

If we assume $c_x=\text{const}$, then we obtain from Table 6-1: for a monoatomic gas $k=1.66$; for a diatomic gas $k=1.4$, for tri- and polyatomic gases $k=1.33$.

With $c_x \neq \text{const}$, for ideal gases the quantity k depends on temperature which follows from the formula

$$k = c_p/c_v = (c_v + R)/c_v = 1 + R/c_v.$$

Mayer's relation yields the following relations for the heat capacities c_v and c_p

$$c_v = R/(k-1); \quad c_p = kR/(k-1). \tag{6-29}$$

6-7. Determination of q_v and q_p for Ideal Gases from Heat-Capacity Tables

As was already pointed out above the quantity of heat involved in an isobaric and isochoric process of an ideal gas can be calculated by the following formula

$$q_{p,\,1\text{-}2} = c_{pm}\Big|_0^{t_2} t_2 - c_{pm}\Big|_0^{t_1} t_1 = i_2 - i_1; \tag{6-30}$$

$$q_{v,\,1\text{-}2} = c_{vm}\Big|_0^{t_2} t_2 - c_{vm}\Big|_0^{t_1} t_1 = u_2 - u_1. \tag{6-31}$$

Hence, to determine the amounts of heat q_p and q_v, we must know either the heat capacities in the temperature interval from 0 to t °C or the values of the enthalpies and internal energies.

At the present time there are a great number of handbooks and special tables in which these values are given with a high degree of accuracy for a wide range of temperatures. The latest data on heat capacities, enthalpy and internal energy have been calculated using the more accurate spectroscopic constants determined by the method of quantum statistics. The above presented Einstein's formula for heat capacity can be considered as the first step in the creation of a modern quantum theory of heat capacity.

In literature published in USSR, detailed data on heat capacities c_p and c_v and also on enthalpy and internal energy can be found in [2, 10, 12].

6-8. Heat Capacity of Mixtures of Ideal Gases

In calculations for heat installations, mixtures of gases have to be handled, while tables contain values of heat capacities only for individual ideal gases; it is, therefore, expedient to be able to determine the heat capacity of a mixture of gases. If a gas mixture is given in mass fractions, then the mass heat capacity of the mixture is determined as the sum of the products of the mass fractions by the mass heat capacity of each gas component

$$c_{v,\,mix} = g_1 c_{v1} + g_2 c_{v2} + \ldots + g_n c_{vn} = \sum_1^n g_i c_{vi} \tag{6-32}$$

and

$$c_{p,\,mix} = g_1 c_{p1} + g_2 c_{p2} + \ldots + g_n c_{pn} = \sum_1^n g_i c_{pi}, \tag{6-33}$$

where $g_1, g_2, \ldots, g_n$ are the mass fractions of each component of the gas mixture.

If a mixture of gases is given in volume fractions, then the volume heat capacity of the mixture is equal to the sum of the products of the volume fractions by the volume heat capacity of each component gas

$$c'_{v,\,mix}=r_1c'_{v1}+r_2c'_{v2}+\ldots+r_nc'_{vn}=\sum_1^n r_ic'_{vi} \tag{6-34}$$

and

$$c'_{p,\,mix}=r_1c'_{p1}+r_2c'_{p2}+\ldots+r_nc'_{pn}=\sum_1^n r_ic'_{pi}, \tag{6-35}$$

where $r_1, r_2, \ldots, r_n$ are the volume fractions of each component of the mixture of gases.

The molar heat capacity of a mixture of gases is equal to the sum of the products of the volume fractions by the molar heat capacities of the gas mixture components

$$\mu c_{v,\,mix}=r_1\mu_1c_{v1}+r_2\mu_2c_{v2}+\ldots+r_n\mu_nc_{vn}=\sum_1^n r_i\mu_ic_{vi},$$

and

$$\mu c_{p,\,mix}=r_1\mu_1c_{p1}+r_2\mu_2c_{p2}+\ldots+r_n\mu_nc_{pn}=\sum_1^n r_i\mu_ic_{pi},$$

where μ = average molecular mass of the mixture of gases;
$\mu_1, \mu_2, \ldots, \mu_n$ = molecular masses of individual gas components.

If the density and the specific volume of a mixture of gases under standard physical conditions are known, the mass heat capacity of the mixture can be determined by the formulae

$$c_{v,\,mix}=c'_{v,\,mix}v_{mix,\,0^\circ}=c'_{v,\,mix}/\varrho_{mix,\,0^\circ}$$

and

$$c_{p,\,mix}=c'_{p,\,mix}v_{mix,\,0^\circ}=c'_{v,\,mix}/\varrho_{mix,\,0^\circ}.$$

6-9. Approximate Values of Heat Capacities*

For approximate calculations use is sometimes made of empirical formulae allowing for the linear dependence of heat capacity on temperature. When applied to the true heat capacity, the linear dependence of heat capacity on temperature can be expressed by the equation

$$c_x=a+bt, \tag{6-36}$$

* In designing equipment and machines for the food industry, the average heat capacity is calculated by formula (6-37).

where a= true heat capacity at 0 °C;

b = slope of the straight line characterizing the change in heat capacity with temperature.

Knowing the dependence $c_x=f(t)$, Eq. (6-25) can be used to determine the average heat capacity c_{xm}

$$c_{xm}\Big|_{t_1}^{t_2}=\frac{1}{t_2-t_1}\int_{t_1}^{t_2} c_x\,dt=\frac{1}{t_2-t_1}\int_{t_1}^{t_2}(a+bt)\,dt=\frac{1}{t_2-t_1}\left[a(t_2-t_1)+b\,\frac{t_2^2-t_1^2}{2}\right]=$$

$$=a+\frac{b}{2}(t_2+t_1). \qquad (6\text{-}37)$$

The equations for the average mass and volume heat capacities of gases in the temperature interval from 0° to 1500 °C are given in the Appendix, Table XIV.

TABLE 6-2

Gas	Chemical formula	Heat capacities				$k=\frac{c_p}{c_v}$
		molar, kJ/kmole·deg		mass, kJ/kg·deg		
		μc_p	μc_v	c_p	c_v	
Helium	He	20.93	12.60	5.237	3.161	1.660
Hydrogen	H_2	28.62	20.30	14.200	10.070	1.410
Air	—	29.07	20.76	1.004	0.716	1.401
Methane	CH_4	34.74	26.42	2.165	1.647	1.315
Ammonia	NH_3	35.00	26.67	2.056	1.566	1.313

Heat capacities for some gases in the ideal state (at $p\to 0$ and $t=0$ °C) are given in Table 6-2.

6-10. Entropy. Calculation of Entropy of an Ideal Gas for Reversible and Irreversible Processes

As was already mentioned, heat q is not a function of state and $dq=du+p\,dv$ will not be a total differential; dq is but some infinitely small quantity. In order to integrate the right-hand side of the equation stating mathematically the first law of thermodynamics, $dq=du+p\,dv$, the dependence of p on v (or of p on T) must be known. Elementary calculus proves that a differential binomial can always be converted into a total differential by dividing (or multiplying) it by an integrating divider (denominator). For an elementary quantity of heat dq such an integrating divider is the absolute temperature T K.

Let us demonstrate it by considering an ideal gas. We have $dq=c_v\,dT+p\,dv$, or, replacing p with RT/v, we obtain $dq=c_v\,dT+RT\,dv/v$.

Dividing both sides of the above equation by T, we find that

$$dq/T = c_v\, dT/T + R\, dv/v. \qquad (6\text{-}38)$$

It follows from Eq. (6-38) that when the state of a gas is reversible the expression dq/T is the total differential of some function of variables T and v (c_v depends only on temperature and R is a constant quantity). R. Clausius has given this function the name of entropy and denoted it by S. The total entropy S is measured in units of J/deg, and the specific entropy—in units of J/kg·deg.

Thus, for a gas undergoing a reversible process of change in state the differential of entropy is

$$ds = dq/T. \qquad (6\text{-}39)$$

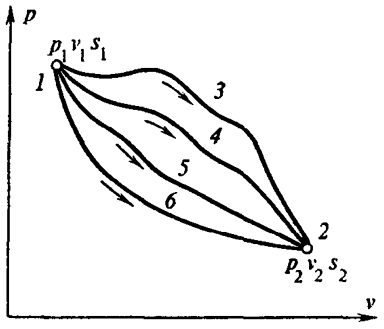


FIG. 6-2

Entropy is a single-valued (unambiguous) function of the state of a gas, acquiring for each of its states a rather definite value. Entropy is an extensive (depends on the mass of substance) parameter of state and its change in any thermodynamic process is fully determined by the extreme states of the body involved and is independent of the path of the process. Accordingly, the entropy of a gas, being a property of state, changes in the same way in the processes *1-3-2*, *1-4-2*, *1-5-2* and *1-6-2* (Fig. 6-2). This property is true for both irreversible and reversible processes. That is why

$$\Delta s_{1\text{-}3\text{-}2} = \Delta s_{1\text{-}4\text{-}2} = \Delta s_{1\text{-}5\text{-}2} = \Delta s_{1\text{-}6\text{-}2} = s_2 - s_1 = f(p_2 v_2) - f(p_1 v_1).$$

Since entropy possesses the property of additivity, the algebraic sum of the changes in the entropy of individual bodies, composing a thermodynamic system will be equal to the change in entropy of the thermodynamic system as a whole, and, depending on the processes, the change in the entropy of individual bodies can be represented by both positive and negative quantities.

Entropy can be defined as the function of the basic properties of state

$$s = f_1(p, v); \quad s = f_2(p, T); \quad s = f_3(v, T).$$

The total differentials of entropy have the appearance

$$\left.\begin{aligned} ds &= (\partial s/\partial p)_v\, dp + (\partial s/\partial v)_p\, dv, \\ ds &= (\partial s/\partial p)_T\, dp + (\partial s/\partial T)_p\, dT, \\ ds &= (\partial s/\partial v)_T\, dv + (\partial s/\partial T)_v\, dT. \end{aligned}\right\} \qquad (6\text{-}40)$$

The partial derivatives of entropy present in Eqs. (6-40) are calculated by the equations derived in Chapter Ten.

To obtain the change in entropy expressed as a function of T and v, Eq. (6-38) is presented in the following form

$$ds = c_v\, dT/T + R\, dv/v. \tag{6-41}$$

Integrating with $c_v = \text{const}$, we find for an ideal gas that

$$s_2 - s_1 = c_v \ln T_2/T_1 + R \ln v_2/v_1. \tag{6-42}$$

To express the change in entropy as a function of T and p, volume v must be eliminated from Eq. (6-41). Upon differentiation, Clapeyron's equation yields

$$pv = RT; \quad p\, dv + v\, dp = R\, dT; \quad dv/v = dT/T - dp/p.$$

Substituting the value of dv/v into Eq. (6-41), we obtain

$$ds = c_v\, dT/T + R\, dT/T - R\, dp/p = c_p\, dT/T - R\, dp/p.$$

Integrating, and assuming $c_p = \text{const}$, we find that

$$s_2 - s_1 = c_p \ln T_2/T_1 - R \ln p_2/p_1. \tag{6-43}$$

To find the change in entropy expressed as a function of p and v, temperature T must be eliminated from Eq. (6-41). Applying the same method, we obtain

$$ds = c_v\, dv/v + c_v\, dp/p + R\, dv/v,$$

whence

$$ds = (c_v + R)\, dv/v + c_v\, dp/p = c_p\, dv/v + c_v\, dp/p.$$

Integrating, we find that

$$s_2 - s_1 = c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{p_2}{p_1}. \tag{6-44}$$

Considering that the change in the entropy of a body does not depend on the nature of the process the body undergoes, the derived Eqs. (6-42) through (6-44) are applicable both to reversible and irreversible processes.

Equation (6-39) can be used to derive a general calculation formula for heat capacity.

The heat capacity c_x of any process is equal to the product of absolute temperature T by the partial derivative of entropy s with respect to temperature T at $x = \text{const}$:

$$c_x = T\left(\frac{\partial s}{\partial T}\right)_x. \tag{6-45}$$

Substituting into Eqs. (5-9) and (5-13) the value of dq from Eq. (6-39), we obtain

$$T\, ds = du + p\, dv, \tag{6-46}$$

$$T\, ds = di - v\, dp. \tag{6-47}$$

The equalities (6-46) and (6-47) contain only the parameters of state and their differentials and are referred to as *thermodynamic identities;* they relate to reversible processes.

If in a thermodynamic system, in addition to the work of expansion (change in volume), work dl_φ, not associated with the change in volume of the body is performed, the thermodynamic identities acquire the following appearance

$$T\,ds = du + p\,dv + dl_\varphi; \tag{6-48}$$

$$T\,ds = di - v\,dp + dl_\varphi. \tag{6-49}$$

In thermodynamics internal energy, enthalpy, entropy and heat capacities are referred to as the *caloric properties of substance*, and specific volume, absolute pressure and temperature are known as the *thermal properties of substance.*

6-11. T-s Diagram of State

Entropy can be used together with one of the main parameters of state for a graphical representation of thermodynamic processes. For this purpose it is most convenient to use entropy and absolute temperature T. If entropy s is plotted on the abscissa, or x-axis, and absolute temperature—on the ordinate, or y-axis, we obtain a T-s system of coordinates, i.e. a T-s diagram, on which the state of a gas is represented by a point, and the process—by a curve whose equation can be presented as $T=f(s)$. The elementary heat of the process $dq=T\,ds$ is represented on the diagram by the elementary area of height T and base ds (Fig. 6-3). The magnitude of the area under the curve of the reversible process *1-3-2* represents on the same scale the heat added in the process

$$q_{1\text{-}2} = \text{area } 513\,265 = \int_1^2 T\,ds.$$

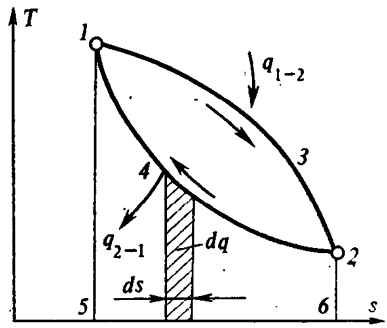


FIG. 6-3

On the T-s diagram the area confined within the line of the process, extreme ordinates and the s-axis represents to some scale the heat involved in the process depicted.

It follows from equation $dq=T\,ds$ that dq and ds have the same signs. If entropy s increases in the process, it means that heat is added, or transferred, to the gas. If entropy s diminishes, it indicates that heat is being rejected (transferred) from the working medium.

A reversible cyclic process is represented on the T-s diagram by the area *13241* confined by the two curves of the process.

In accordance with the first law of thermodynamics, the difference between the added and rejected heat represents the useful external work performed by 1 kg of a working medium, undergoing a cyclic reversible process, on the surrounding medium

$$q_{1\text{-}2}-q_{2\text{-}1}=l'=\oint T\,ds=\oint dq=\oint dl'.$$

Thus, on the *T-s* diagram the specific work done by the working medium undergoing a reversible cyclic process is equal numerically to the area confined by the closed line of the cycle and gives a clear indication of the change in the temperature of the working medium.

For ideal gases entropy is arbitrarily assumed to be equal to zero under standard physical conditions.

In conclusion it should be noted that the concept of entropy has been introduced as applied to an ideal gas and all statements concerning the properties of entropy cannot as yet be assumed to be valid for real gases as well. However, as will be shown in Chapter 8, the concept of entropy can be elucidated with sufficient accuracy irrespective of the properties of the working medium. Meanwhile this parameter will be used as the most convenient in analyzing the ideal gas properties.

Typical Questions and Examples to Chapter Six

1. What is the definition of specific heat capacity?
2. Give the definitions of the mass, volume and molar heat capacities.
3. In what units is heat capacity measured?
4. What is meant by true heat capacity?
5. What is the definition of the average heat capacity?
6. Write down the equation for the quantity of heat in terms of the average heat capacity.
7. How is the average heat capacity in the temperature interval from t_1 to t_2 determined, using heat-capacity tables compiled for a temperature range from 0 to t °C?
8. What is the difference between the heat capacities of ideal and real gases?
9. What is meant by the heat capacity at a constant volume and by the heat capacity at a constant pressure?
10. Why is the constant-pressure heat capacity always greater than the constant-volume heat capacity?
11. Explain the meaning of all quantities in Mayer's relation.
12. Explain the meaning of the quantity k. How is it determined?
13. How are q_v and q_p determined from the tables of heat capacity?
14. Write down the equations for the mass, volume and molar heat capacities of mixtures of gases.
15. What function is referred to as entropy?
16. Determine the increase of entropy of an ideal gas depending on the main parameters of state.

17. What does the area under the curve of a process presented graphically on a *T-s* diagram represent?

Example 6-1. Air at a pressure $p_1=10$ bar and volume $V=0.4$ m³, and a temperature $t_1=127$ °C is heated at a constant volume to a temperature of 327 °C. Determine the mass of the air, the final pressure and the amount of heat transferred to the heated air.

The mass of air is determined from Clapeyron's equation

$$m=\frac{pV}{RT}=\frac{10\times10^5\times0.4}{287.04\times400}=3.5 \text{ kg}$$

The final pressure

$$p_2=\frac{p_1T_2}{T_1}=\frac{10\times600}{400}=15 \text{ bar.}$$

From the tables we determine the average mass heat capacities of air

$$c_{vm}\Big|_0^{t_2}=0.744 \text{ kJ/kg·deg} \quad \text{and} \quad c_{vm}\Big|_0^{t_1}=0.721 \text{ kJ/kg·deg.}$$

The amount of heat transferred (added) to the air

$$Q=m\left(c_{vm}\Big|_0^{t_2}t_2-c_{vm}\Big|_0^{t_1}t_1\right)=3.5\times150.6=527 \text{ kJ.}$$

Example 6-2. A current of cold air at a temperature of 10 °C is mixed with a current of hot air at a temperature of 1000 °C; the temperature of the mixture is 100 °C. Determine the mass fractions of the cold and hot air, assuming the pressure of the cold and hot air and of the mixture of air to be the same.

The mass fractions

$$g_1+g_2=1 \quad \text{and} \quad g_2=1-g_1.$$

The heat balance equation

$$g_1c_{pm1}t_1+(1-g_1)c_{pm2}t_2=c_{pm}t \quad \text{or} \quad g_1i_1+(1-g_1)i_2=i,$$

whence

$$g_1=(i-i_2)/(i_1-i_2).$$

Substituting the values of the enthalpies of air, found from Table XIII in the Appendix, into the above equation,

$$g_1=(i-i_2)/(i_1-i_2)=(105-1090)/(10.5-1090)=0.917;$$

$$g_2=1-0.917=0.083.$$

1 kg of the mixture comprises 0.917 kg of cold air and 0.083 kg of hot air.

Example 6-3. A quantity of heat $q_p=500$ kJ/kg is transferred to 1 kg of air at a constant pressure. Find the temperature t_2 if $t_1=20$ °C.

From Eq. (5-19) we find the enthalpy $i_2=q_p+t_1$. From table XIII in the Appendix we find $i_1=20.8$ kJ/kg. Therefore, $i_2=500+20.8=520.8$ kJ/kg. From Table XIII in the Appendix we find that $t_2=500$ °C.

Example 6-4. Determine the change in entropy of 1 kg of O_2 in a process of expansion. The initial parameters of the oxygen O_2 are: $t_1=300$ °C, $p_1=3.0$ MN/m² ($p_1=30$ bar); the final parameters: $t_2=400$ °C, $p_2=0.4$ MN/m² ($p_2=4$ bar). Calculate for two cases:

(1) for constant heat capacity; (2) for variable heat capacity.

1. The change of entropy for constant heat capacity

$$s_2-s_1=c_p \ln \frac{T_2}{T_1}-R \ln \frac{p_2}{p_1}=0.945\times 2.303 \log \frac{313}{573}-$$

$$-0.2598\times 2.303 \log \frac{4}{30}=-0.57+0.523=-0.047 \text{ kJ/kg·deg},$$

where

$$c_p=\frac{k}{k-1}R=\frac{1.4}{0.4}\times 0.2598=0.945 \text{ kJ/kg·deg}.$$

2. The change of entropy, found from Table XIII in the Appendix (for variable heat capacity), is

$$s_2-s_1=s_2^{table}-s_1^{table}-R \ln p_2/p_1=0.1252-0.6958+0.523=$$

$$=-0.0476 \text{ kJ/kg·deg}$$

The formula determining the change of entropy for variable heat capacity yields more accurate results.

CHAPTER SEVEN

MAIN THERMODYNAMIC PROCESSES IN IDEAL GASES

7-1. General Investigation Problems

The first law of thermodynamics interrelates the quantity of heat, the change in internal energy and the external work performed by a gas with the amount of heat transferred to the body or removed from it depending on the nature of the process.

The main processes that are of paramount importance both for theoretical investigations and practical engineering applications include: the *isochoric* process, proceeding at a constant volume; the *isobaric* process, occurring at a constant pressure; the *isothermal* process, taking place at a constant temperature; and the *adiabatic*, proceeding without heat transfer to and from the surrounding medium.

In addition, there exist a group of processes which under certain conditions are generalized ones for the basic processes. These processes are referred to as *polytropic* and they are characterized by a constant heat capacity.

All processes are studied applying one common investigation method consisting in the following:

the equation of the curve of the process is derived and presented graphically on the p-v and T-s diagrams;

the relation is established between the main properties of the working medium at the beginning and end of the process investigated;

the change in internal energy is determined by means of the formula true for all processes of an ideal gas

$$\Delta u = u_2 - u_1 = \int_{t_1}^{t_2} c_v \, dt = c_{vm}\Big|_0^{t_2} t_2 - c_{vm}\Big|_0^{t_1} t_1,$$

or at a constant heat capacity

$$u_2 - u_1 = c_v(t_2 - t_1);$$

the work done to change the volume of the gas is calculated by formula

$$l = \int_{v_1}^{v_2} p \, dv = \int_{v_1}^{v_2} f(v) \, dv;$$

the quantity of heat in the process is determined by formula

$$q_{1\text{-}2}=\int_{t_1}^{t_2} c_x\,dt=c_{xm}\Big|_0^{t_2} t_2-c_{xm}\Big|_0^{t_1} t_1;$$

the change of enthalpy in the process is determined by the formula true for all processes that an ideal gas undergoes

$$i_2-i_1=c_{pm}\Big|_0^{t_2} t_2-c_{pm}\Big|_0^{t_1} t_1,$$

or for a constant heat capacity

$$i_2-i_1=c_p(t_2-t_1);$$

the change of the entropy of an ideal gas is determined by formulae

$$s_2-s_1=c_v \ln T_2/T_1+R \ln v_2/v_1,$$
$$s_2-s_1=c_p \ln T_2/T_1-R \ln p_2/p_1.$$

The investigated processes are considered to be reversible.

7-2. The Isochoric Process

A process that occurs at constant volume is called an *isochoric* process ($dv=0$, or $v=\text{const}$). The curve representing the process on a T-v diagram is called an *isochor*. The process is presented graphically in Fig. 7-1. From the equation of state of an ideal gas, $pv=RT$ at $v=\text{const}$, we obtain

$$p/T=R/v=f(v)=\text{const}.$$

At a constant volume the pressure of a gas changes in direct proportion to absolute temperatures

$$p_1/p_2=T_1/T_2. \qquad (7\text{-}1)$$

At $v=\text{const}$ the external work, performed by a gas on the surrounding medium, is equal to zero, since $dv=0$. Hence

$$l=\int_{v_1}^{v_2} p\,dv=0.$$

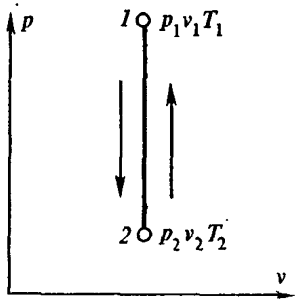


FIG. 7-1

The available (useful) external work l', that can be transferred to the surrounding medium (object of work) is equal to

$$l'=-\int_{p_1}^{p_2} v\,dp=-v(p_2-p_1).$$

From the derived expression it is clear that the useful external work l' done in an isochoric process is equal to the work of displacement $l'=p_1v-p_2v$. For instance, the work done to displace an incompressible liquid along a channel from one section to another.

At $dl=0$ the main mathematical statement, or equation, of the first law of thermodynamics acquires the appearance

$$dq_v=du_v=c_v\,dt.$$

The quantity of heat involved in processes taking place at constant heat capacity is equal to

$$q_{v,\,1\text{-}2}=\int_{t_1}^{t_2}(\partial u/\partial t)_v\,dt=\int_{t_1}^{t_2}c_v\,dt=c_v(t_2-t_1)=u_2-u_1.$$

The entire heat transferred from the surrounding medium is spent only to change the internal energy of the working medium.

At constant heat capacity in the process *1-2*

$$q_{v,\,1\text{-}2}=u_2-u_1=c_{vm}\Big|_0^{t_2}t_2-c_{vm}\Big|_0^{t_1}t_1. \tag{7-2}$$

If the process *1-2* takes place with an increase in pressure, heat is transferred to the working medium and this results in an increase in the internal energy and temperature of the gas. If the pressure drops in a process, heat is transferred from the working medium to the surrounding medium, the internal energy and temperature of the gas diminish (Fig. 7-1).

The change of entropy in a reversible isochoric process is determined from Eq. (6-42)

$$s_2-s_1=c_v\ln T_2/T_1+R\ln v_2/v_1,$$

but at $v=\text{const}$ $\ln v_2/v_1=0$, therefore, the change of entropy at a constant heat capacity is equal to

$$s_2-s_1=\int_{T_1}^{T_2}(\partial s/\partial T)_v\,dT=c_v\ln T_2/T_1=c_v\ln p_2/p_1. \tag{7-3}$$

As is clear from Eq. (7-3) on the *T-s* diagram the isochor is represented by the curve *1-2* (Fig. 7-2). The subtangent to the curve *1-2*, drawn at any of its points, gives the value of the true heat capacity c_v.

In fact, it follows from analytical isometry that the magnitude of the subtangent at point *2*

$$3\text{-}4=T(ds/dt)=dq_v/dT=c_v.$$

The area *31243* represents on a certain scale the quantity of heat q_v that is expended in the process *1-2* to change the internal energy of the gas (u_2-u_1) undergoing the process.

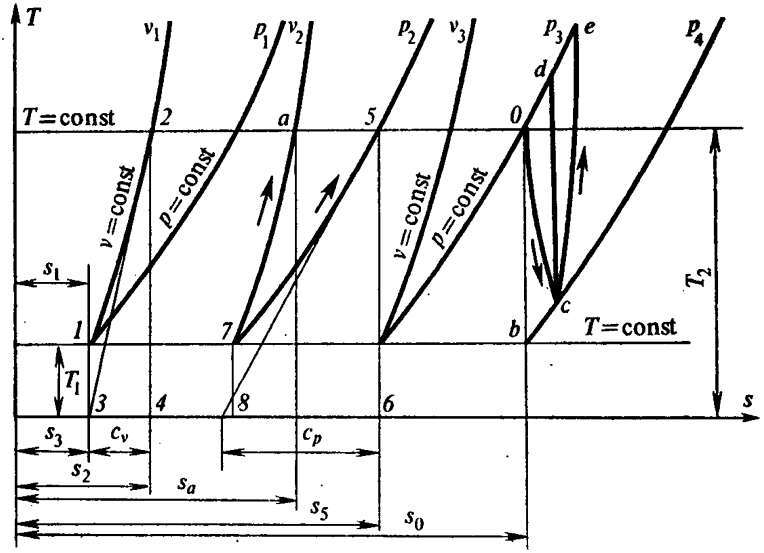


FIG. 7-2

The isochors representing various volumes are equidistant curves, possessing the same angular coefficients at the same temperature.

The isochors plotted for different volumes are spaced at a distance from one another which is determined from Eq. (6-42) at $T=\text{const}$ (Fig. 7-2)

$$\Delta s = s_a - s_2 = R \ln v_a/v_2.$$

The larger the volume of the gas, the greater the distance between the isochor and the ordinate axis.

7-3. The Isobaric Process

A process that occurs at constant pressure is referred to as an *isobaric* process in the course of which $dp=0$ or $p=\text{const}$. The curve representing the process on a p-v diagram is called an *isobar*. The isobaric process is represented graphically in Fig. 7-3.

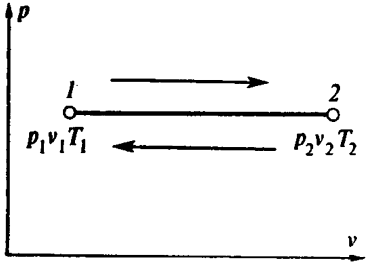


FIG. 7-3

From the equation of state of an ideal gas, written for an isobaric process, we find that

$$v/T = R/p = \varphi(p) = \text{const}.$$

The above relationship is called the *Gay-Lussac law*. For the process *1-2* shown in Fig. 7-3

$$v_1/v_2 = T_1/T_2 = \varrho_2/\varrho_1. \qquad (7\text{-}4)$$

In an isobaric process the volumes of the same amount of gas change in direct proportion to absolute temperatures.

The temperature of the gas rises upon expansion and falls upon compression.

The specific work performed due to the change in volume is expressed by the following equation

$$l=p\int_{v_1}^{v_2} dv=p(v_2-v_1), \tag{7-5}$$

or

$$l=R(T_2-T_1)=R(t_2-t_1). \tag{7-6}$$

The available (useful) external work

$$l'=-\int_1^2 v\,dp=0.$$

At $p=\text{const}$ ($dp=0$) the main mathematical statement of the first law of thermodynamics takes the following form

$$dq_p=c_p\,dt=di.$$

Consequently, the amount of heat transferred to the working medium undergoing an isobaric process at a constant heat capacity is equal to

$$q_{p,\,1\text{-}2}=\int_{t_1}^{t_2}(\partial i/\partial t)_p\,dt=\int_{t_1}^{t_2}c_p\,dt=c_p(t_2-t_1)=i_2-i_1. \tag{7-7}$$

and at a variable heat capacity

$$q_{p,\,1\text{-}2}=\int_{t_1}^{t_2}c_p\,dt=c_{pm}\Big|_0^{t_2}t_2-c_{pm}\Big|_0^{t_1}t_1=i_2-i_1. \tag{7-8}$$

A part of the heat transferred to the working medium, equal to $p(v_2-v_1)$, is converted into the work of expansion, and the other part is expended to increase the internal energy of the body.

For a reversible isobaric process occurring at constant heat capacity the change of entropy is found from Eq. (6-43)

$$s_2-s_1=c_p\ln\frac{T_2}{T_1}-R\ln\frac{p_2}{p_1},$$

but at $p=\text{const}$ $\ln p_2/p_1=0$, therefore

$$s_2-s_1=\int_{T_1}^{T_2}\left(\frac{\partial s}{\partial T}\right)_p dT=\int_{T_1}^{T_2}\left(\frac{c_p}{T}\right)dT=c_p\ln\frac{T_2}{T_1}=c_p\ln\frac{v_2}{v_1}. \tag{7-9}$$

On a *T-s* diagram an isobar is represented by curve *7-5* (Fig. 7-2) and, just like the isochor, the convexity of the curve faces downward. The subtangent to the curve at any of its points gives the value of the true heat capacity c_p. For point *5* the subtangent

$$8\text{-}6 = T(ds/dT) = dq_p/dT = c_p.$$

The area *87568* under the isobar represents on a certain scale the quantity of heat q_p transferred to the gas, equal to the change in enthalpy, $i_2 - i_1$, in the process.

All isobars are equidistant curves, having the same angular coefficients or slopes at the same temperature. The horizontal distance between the isobars representing isobaric processes taking place at different pressures is determined from Eq. (6-43) at $T = \text{const}$ (see Fig. 7-2)

$$\Delta s = s_0 - s_5 = R \ln p_5/p_0.$$

It follows from the above equation that the distance between the isobars depends on the magnitude of pressure and nature of the gas involved. The greater the pressure of the gas, the closer is the isobar to the ordinate axis.

A comparison of Eqs. (7-3) and (7-9) indicates that when isochoric and isobaric processes are realized in the same temperature interval, entropy shall increase at a greater rate in the isobaric process, since c_p is always greater than c_v. Isobars are flatter curves than isochors (Fig. 7-2).

7-4. The Isothermal Process

A process that occurs at constant temperature is said to be an *isothermal* process in the course of which $T = \text{const}$ or $dT = 0$. The curve representing the process is called an *isotherm* (Fig. 7-4).

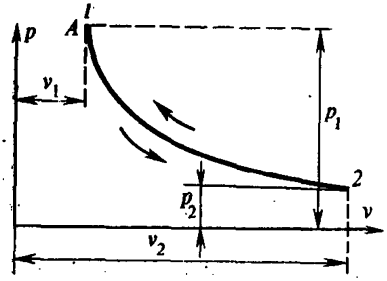


FIG. 7-4

For an ideal gas undergoing an isothermal process

$$pv = RT = \psi(T) = \text{const}$$

or

$$p_1v_1 = p_2v_2 \quad \text{and} \quad p_1/p_2 = v_2/v_1. \qquad (7\text{-}10)$$

At a constant temperature the volume of the gas changes in inversely proportion to its pressure (Boyle's law).

On a *pv*-diagram the isothermal process is represented by an equilateral hyperbola. At $T = \text{const}$ the main mathematical statement of the first law of thermodynamics takes the simple form

$$dq = dl \quad \text{and} \quad q_{1\text{-}2} = l_{1\text{-}2}.$$

The quantity of heat transferred to the working medium is numerically equal to the work spent to change the volume.

Knowing the equation of the isothermal process for an ideal gas, we can calculate the work associated with the process. The specific work done to change the volume is equal to

$$l=\int_{v_1}^{v_2} p\,dv,$$

but from the equation of the isotherm we have

$$pv=p_1v_1 \quad \text{or} \quad p=p_1v_1/v,$$

therefore,

$$l=p_1v_1\int_{v_1}^{v_2} dv/v.$$

Integrating the above equation, we obtain

$$l=p_1v_1 \ln v_2/v_1=q. \tag{7-11}$$

Equation (7-11) determines the work done and the external heat of an ideal gas. Passing to common, or Brigg's, logarithms, we have

$$q=l=2.3\,p_1v_1 \log v_2/v_1=2.3\,p_1v_1 \log p_1/p_2=$$
$$=2.3\,RT \log v_2/v_1=2.3\,RT \log p_1/p_2. \tag{7-12}$$

The available specific external work l' is determined by formula

$$l'=-\int_{p_1}^{p_2} v\,dp=p_1v_1\int_{p_2}^{p_1} dp/p=p_1v_1 \ln p_1/p_2, \tag{7-13}$$

i.e. when an ideal gas undergoes an isothermal process $l'=l=q$, or the work spent to change the volume, the available (useful) work and the amount of heat transferred to the working medium are equal to one another.

In an isothermal process the heat capacity

$$c_T=dq/dt=dq/0=\pm\infty.$$

The enthalpy and internal energy of the ideal gas do not change, i.e. $di=0$ and $du=0$.

On a T-s diagram the isothermal process is presented by a curve running parallel to the s-axis, as shown in Fig. 7-2. The change of entropy can be determined using Eq. (6-42)

$$s_2-s_1=c_v \ln \frac{T_2}{T_1}+R \ln \frac{v_2}{v_1},$$

whence

$$s_2-s_1=R\ln\frac{v_2}{v_1} \quad \text{and} \quad s_2-s_1=R\ln\frac{p_1}{p_2}. \tag{7-14}$$

The heat involved in an isothermal process is equal to the product of the change in entropy (s_2-s_1) and absolute temeperature T:

$$q=T(s_2-s_1).$$

7-5. The Adiabatic Process

A process during which no heat is transferred to or abstracted, i.e. in the absence of heat exchange with the surrounding medium, is referred to as an *adiabatic* process, and the curve representing such a process is called an *adiabatic curve*. For an adiabatic process to be realized the necessary condition is $dq=0$ and, consequently, $q=0$.

A reversible adiabatic process can be realized in a cylinder with ideally, or absolutely, heat-insulated walls with the piston travelling at an infinitely low velocity.

Let us derive the equation of the adiabatic curve. At $dq=0$ the equation of the first law of thermodynamics yields

$$c_p\,dT-v\,dp=0 \quad \text{and} \quad c_v\,dT+p\,dv=0.$$

Dividing the first equation by the second, we obtain

$$\frac{c_p\,dT}{c_v\,dT}=-\frac{v\,dp}{p\,dv} \quad \text{or} \quad k\frac{dv}{v}=-\frac{dp}{p}.$$

Integrating the last equation on condition that $k=\text{const}$ ($c_p=\text{const}$ and $c_v=\text{const}$), we find that

$$k\int_{v_1}^{v_2}\frac{dv}{v}=-\int_{p_1}^{p_2}\frac{dp}{p} \quad \text{and} \quad k\ln\frac{v_2}{v_1}=\ln\frac{p_1}{p_2}.$$

Taking the antilogarithms, we obtain

$$(v_2/v_1)^k=p_1/p_2, \quad \text{or} \quad p_1v_1^k=p_2v_2^k,$$

whence the equation of the adiabat is

$$pv^k=\text{const}. \tag{7-15}$$

For an adiabatic process the product of pressure and the volume of a gas to the power k is constant. The quantity k is called the *adiabatic exponent*. Let us consider the relation between the main properties of a gas undergoing an adiabatic process.

It follows from the equation of the adiabatic curve that

$$\frac{p_1}{p_2}=\left(\frac{v_2}{v_1}\right)^k \quad \text{and} \quad \frac{v_2}{v_1}=\left(\frac{p_1}{p_2}\right)^{\frac{1}{k}}.$$

Substituting these ratios of the parameters of state into the equation for the extreme points of the process $(p_2/p_1)\cdot(v_2/v_1)=(T_2/T_1)$, and upon corresponding transformations, we find that

$$\frac{T_1}{T_2}=\left(\frac{v_2}{v_1}\right)^{k-1}=\left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}}.$$

The specific work due to a change in volume, $l=\int_{v_1}^{v_2} p\,dv$, done by the working medium on the surroundings in an equilibrium adiabatic process, can be calculated by the equation of the adiabat

$$p=p_1v_1^k/v^k$$

or

$$l=\int_{v_1}^{v_2} p_1v_1^k\left(\frac{dv}{v^k}\right)=\left[\frac{p_1v_1^k}{1-k}\right](v_2^{1-k}-v_1^{1-k})=$$

$$=\frac{p_1v_1^k}{k-1}\left(\frac{1}{v_1^{k-1}}-\frac{1}{v_2^{k-1}}\right)=\frac{1}{k-1}\left(\frac{p_1v_1^k}{v_1^{k-1}}-\frac{p_2v_2^k}{v_2^{k-1}}\right),$$

whence

$$l=[1/(k-1)](p_1v_1-p_2v_2). \qquad (7\text{-}16)$$

From expression (7-16) the following formulae can be derived

$$l=[p_1v_1/(k-1)](1-T_2/T_1); \quad l=[R/(k-1)](T_1-T_2).$$

The ratio of temperatures is replaced with the ratio of volumes and pressures

$$l=[p_1v_1/(k-1)]\left[1-\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]=[RT_1/(k-1)]\left[1-\left(\frac{v_1}{v_2}\right)^{k-1}\right].$$

All equations relating p, v, T and the equations of work were derived on condition that $k=\text{const}$. When k is variable calculations are usually made with an everage k, corresponding to the variation of temperature in the process and determined by equation

$$k=c_p\Big|_{t_1}^{t_2}\Big/c_v\Big|_{t_1}^{t_2}=\Delta i/\Delta u.$$

For the adiabatic process the equations of the first law of thermodynamics (6-46) and (6-47) have the following appearance

$$du=-p\,dv \quad \text{and} \quad di=v\,dp,$$

whence

$$(\partial u/\partial v)_s=-p \quad \text{and} \quad (di/dp)_s=v.$$

The above relations can be used to obtain

$$(\partial i/\partial u)_s = -(v/p)(\partial p/\partial v)_s.$$

The obtained expression is the differential equation of an isotropic process. In this equation the ratio $(\partial i/\partial u)_s = k$.

In accordance with the first law of thermodynamics the work expended upon a change in volume in an adiabatic process is done at the expense of the loss of internal energy of the body involved; at $c_v = \text{const}$

$$l = u_1 - u_2 = c_v(t_1 - t_2);$$

at $c_v \neq \text{const}$

$$l = c_{vm}\Big|_0^{t_1} t_1 - c_{vm}\Big|_0^{t_2} t_2.$$

If the gas undergoes expansion, its internal energy and temperature diminish; if the gas is compressed, its internal energy increases and the temperature rises.

It follows from expression $c = dq/dT$ that in an adiabatic process proceeding at $dq = 0$ heat capacity is also equal to zero.

Let us calculate the available (useful) external work in an adiabatic process, equal to

$$l' = -\int_{p_1}^{p_2} v\,dp.$$

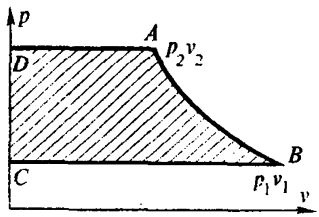


FIG. 7-5

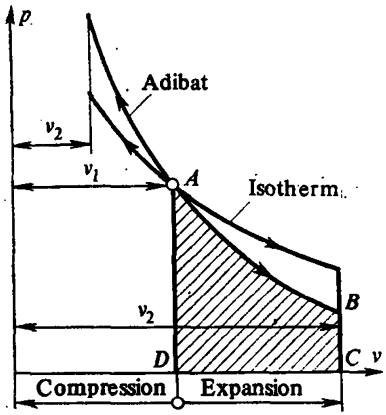


FIG. 7-6

For an ideal gas undergoing a reversible adiabatic process the available external work, or work done on the surrounding medium, is k times greater than the work due to a change in volume, and it has an opposite sign.

In fact, it follows from the equation of an adiabat (7-15) that $k\,dv/v = -dp/p$ or $-v\,dp = kp\,dv$, i.e. $dl' = k\,dl$.

It follows that

$$l' = [k/(k-1)](p_1v_1 - p_2v_2) \qquad (7\text{-}17)$$

and

$$l' = kl.$$

On a p-v diagram the available external work is represented by area $ABCD$ (Fig. 7-5) or by the area confined by the line of the process, extreme abscissas and the p-axis.

It can be seen from Fig. 7-6 that inasmuch as $k>1$ in the equation of the adiabatic curve, the curve runs steeper on the p-v diagram than an isothermal curve.

For a reversible adiabatic process $dq=0$, therefore

$$ds=dq/T=0 \quad \text{and} \quad s_2=s_1=\text{const}, \tag{7-18}$$

i.e. a reversible adiabatic process is simultaneously an isoentropic process (or at a constant entropy) and is depicted on a T-s diagram by a vertical straight line o-b running parallel to the T-axis, as illustrated in Fig. 7-2.

7-6. Polytropic Processes

Up to now processes have been investigated having rather definite symptoms: the isochoric process is realized at a constant volume; the isobaric—at a constant pressure; the isothermal process is realized at a constant temperature; the adiabatic process occurs with no heat transfer between the working medium and the surrounding medium. Along with these processes an infinite multitude of processes can be visualized having other constant symptoms.

Any process involving an ideal gas in which heat capacity is constant is said to be a *polytropic process*, and the curve representing the process graphically is called a *polytrope*.

From the definition of a polytropic process it follows that if the basic thermodynamic processes, the isochoric, isobaric, isothermal and adiabatic, proceed at a constant heat capacity they are special cases of the polytropic process.

The heat capacity of a polytropic process, c_n, can assume the most diverse positive and negative values from $+\infty$ to $-\infty$.

The quantity of heat involved in a polytropic process can be expressed as the product of the heat capacity of the process, c_n, and the temperature difference t_2-t_1 in the initial and final states.

$$q=c_n(t_2-t_1) \quad \text{and} \quad dq=c_n\,dt. \tag{7-19}$$

The equation of a polytropic process is derived from the mathematical statement of the first law of thermodynamics

$$dq=c_n\,dT=c_p\,dT-v\,dp \quad \text{and} \quad dq=c_n\,dT=c_p\,dT+p\,dv.$$

From the above equations we find that

$$(c_n-c_p)/(c_n-c_v)=-v\,dp/p\,dv.$$

Denoting the right-hand side of the above equation by n, we get

$$(c_n-c_p)/(c_n-c_v)=n \quad \text{and} \quad n\,dv/v=-dp/p.$$

Integrating the obtained expression between the limits from the beginning to the end of the process, we find that

$$n \log v_2/v_1=\log p_1/p_2$$

or

$$pv^n = \text{const.} \tag{7-20}$$

Expression (7-20) is the *equation of a polytropic process.*

For each process the *polytropic exponent n* acquires a definite numerical value. For the basic processes: isochoric $n = \pm\infty$, isobaric $n = 0$, isothermal $n = 1$, and for adiabatic processes $n = k$.

Inasmuch as the equation of a polytrope differs form the equation of an adiabat only in the magnitude of the exponent n, it is clear that all equations interrelating the main properties of state can be represented by formulae similar to those of an adiabatic process

$$p_2/p_1 = (v_1/v_2)^n; \quad T_2/T_1 = (v_1/v_2)^{n-1}; \quad T_2/T_1 = (p_2/p_1)^{\frac{n-1}{n}}.$$

For a polytropic process heat capacity is determined from the formula

$$n = (c_n - c_p)/(c_n - c_v), \quad \text{whence} \quad c_n = c_v[(n-k)/(n-1)]. \tag{7-21}$$

Equation (7-21) can be used to determine the heat capacity of a polytropic process for each value of the exponent n.

Substituting into Eq. (7-21) the values of n for the special cases, we obtain the heat capacities for the processes considered:

isochoric process $n = \pm\infty$, $c_n = c_v$;
isobaric process $n = 0$, $c_n = kc_v = c_p$;
isothermal process $n = 1$, $c_n = \pm\infty$;
adiabatic process $n = k$, $c_n = 0$.

The equation for work of change in volume performed by a working medium undergoing a polytropic process is similar to the equation for the work involved in an adiabatic process, i.e.

$$l = [1/(n-1)](p_1v_1 - p_2v_2), \tag{7-22}$$

or

$$l = [RT_1/(n-1)](1 - T_2/T_1) = [p_1v_1/(n-1)]\left[1 - (p_2/p_1)^{\frac{n-1}{n}}\right] =$$
$$= [p_1v_1/(n-1)][1 - (v_1/v_2)^{n-1}]. \tag{7-23}$$

The change of the internal energy of a gas and the quantity of heat in a polytropic process are determined by formulae

$$\Delta u = c_v(t_2 - t_1);$$
$$q = c_n(t_2 - t_1) = c_v[(n-k)/(n-1)](t_2 - t_1). \tag{7-24}$$

By analogy with the adiabatic process, the available external work in a polytropic process amounts to

$$l' = -\int_{p_1}^{p_2} v\,dp = [n/(n-1)](p_1v_1 - p_2v_2) = [n/(n-1)]R(T_1 - T_2). \tag{7-25}$$

The change of enthalpy in a polytropic process

$$i_2-i_1=c_p(t_2-t_1). \tag{7-26}$$

For any polytropic process the value of the polytropic exponent n can be determined by the coordinates of any two points on the curve representing the process

$$n=\frac{\log\frac{p_1}{p_2}}{\log\frac{v_2}{v_1}};\quad n-1=\frac{\log\frac{T_2}{T_1}}{\log\frac{v_1}{v_2}};\quad \frac{n-1}{n}=\frac{\log\frac{T_2}{T_1}}{\log\frac{p_2}{p_1}}. \tag{7-27}$$

Representing a polytropic process in logarithmic coordinates, a simple method can be suggested for determination of the polytropic exponent n. Taking the logarithm of the equation of a polytrope, we obtain

$$\log p+n\log v=\text{const}.$$

This equation is the equation of a straight line plotted on a log p-log v diagram, and the polytropic exponent n represents the slope of the straight line in respect to the x-axis (Fig. 7-7).

The change in the entropy of a gas undergoing a polytropic process is determined by the following formula

$$ds=dq/T=c_n\,dT/T,$$

or for the final change in state

$$s_2-s_1=c_n\ln\frac{T_2}{T_1}=c_v\left[\frac{(n-k)}{(n-1)}\right]\ln\frac{T_2}{T_1}. \tag{7-28}$$

On a T-s diagram the polytropic process is represented by some curve (Fig. 7-8), whose arrangement depends on the exponent n.

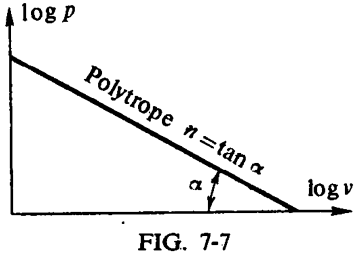


FIG. 7-7

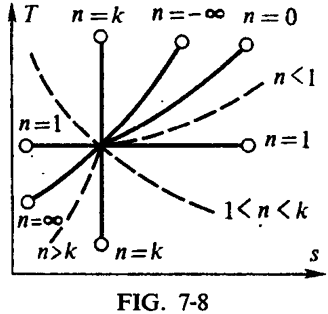


FIG. 7-8

Shown in Fig. 7-9 is the arrangement on a p-v diagram of polytropic processes originating from one point, depending on the polytropic exponent n.

Let us investigate how changes the internal energy of a gas undergoing polytropic processes. In an isothermal process occurring at $n=1$ the internal

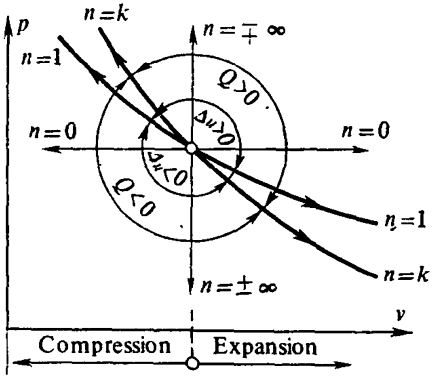


FIG. 7-9

energy of the gas does not change ($u_2=u_1$). In an isobaric process of expansion occurring at $n=0$ the internal energy increases. In an isochoric process with heat addition and occurring with an exponent $n=-\infty$ the internal energy increases. From this it follows that all polytropic processes, i.e. expansion processes, arranged above the isotherm, realized at $n<1$, and processes of compression at $n>1$ proceed with an increase in internal energy. Polytropic processes, i.e. expansion processes, arranged under the isotherm and developing at $n>1$, and processes of compression realized at $n<1$ proceed with a decrease in internal energy.

Let us consider how the sign of the heat involved in polytropic processes changes (Fig. 7-9). In an adiabatic process there is no heat transfer, i.e. heat is neither added nor rejected. In an isothermal ($n=1$), isobaric ($n=0$) processes of expansion and in an isochoric process ($n=-\infty$) heat is added. Consequently, all polytropic processes, i.e. processes of expansion arranged above the adiabat within the limits $k>n>-\infty$, and processes of compression occurring at $\infty>n>k$ proceed with heat transfer to the working medium.

The processes of expansion occurring at $\infty>n>k$, are polytropic, and processes of compression at $-\infty<n<k$ proceed with heat transfer from the working medium, i.e. with rejection of heat.

The heat capacity of processes arranged between an adiabat and an isothermal line is negative, since dq and du have different signs in these processes. Inasmuch as $du=c_v dT$, hence, the sign of du corresponds to that of dT ($du>0$, $dT>0$ and $du<0$, $dT<0$).

Then, it can be seen from the expression $c=dq/dT$ that heat capacity is indeed negative. For all practical purposes this means that when heat is added in these processes there is a drop in temperature, and when heat is rejected, the temperature rises.

Typical Questions and Examples to Chapter Seven

1. Define the main thermodynamic processes.
2. How are an isochor, an isobar, an isotherm and an adiabat represented graphically on a p-v diagram?
3. Write down the equations of the main processes.
4. Write down the formulae relating the parameters of state p, v and T for each process.
5. Explain the rise in temperature upon expansion of a gas undergoing an isobaric process.

6. Prove that in an isobaric process the amount of heat involved is equal to the change in enthalpy.
7. Write down the formulae for the work done upon a change in volume of a gas undergoing main thermodynamic processes.
8. Write down the formulae for available (useful) work for each of the main processes.
9. Why in an adiabatic process does the temperature of the working medium decrease upon expansion and rise upon compression?
10. What is the mutual position on a *p-v* diagram of an isotherm and adiabat drawn from one origin for a gas undergoing expansion and compression?
11. What process is referred to as a polytropic one?
12. Under what conditions shall the main processes of an ideal gas be polytropic?
13. Write down the equation of a polytrope and indicate the limits within which the polytropic exponent n changes.
14. What are the values of the polytropic exponent for the main thermodynamic processes?
15. Write down the equation of heat capacity for a polytropic process and show that this equation can be used to derive the heat capacities for all main thermodynamic processes.
16. In which polytropic processes does the internal energy decrease and in which ones does it increase? Show it on a *p-v* diagram.
17. In which polytropic processes is heat added, or transferred, to the gas and in which ones is heat rejected, or transferred, from the gas?
18. In which polytropic processes and why will heat capacity be negative? What is the physical meaning of it?
19. What equations are used to calculate the change in entropy in isochoric, isobaric, isothermal, adiabatic and polytropic processes?

Example 7-1. A cylinder of volume 0.12 m^3 contains air at absolute pressure of 10×15^5 N/m^2 and temperature of 50 °C. Determine the final pressure, the amount of heat and the change in entropy upon a rise in air temperature to 150 °C.

The mass of air in the cylinder is equal to

$$m=\frac{p_1V}{RT_1}=\frac{10\times10^5\times0.12}{287.04\times323}=1.29 \text{ kg}.$$

The final pressure

$$p_2=\frac{T_2p_1}{T_1}=\frac{423\times10\times10^5}{323}=13.1\times10^5 \text{ N/m}^2.$$

The amount of heat added to the body (air) is

$$Q=m\left(c_{vm}\Big|_0^{t_2}t_2-c_{vm}\Big|_0^{t_1}t_1\right)=1.29(0.722\times150-0.718\times50)=94 \text{ kJ},$$

or

$$Q=m(u_2-u_1)=1.29(108.5-35.9)=94 \text{ kJ}.$$

The change of entropy

$$s_2-s_1=mc_v \ln T_2/T_1=1.29\times0.72\times2.3 \log 423/323=0.252 \text{ kJ/deg}.$$

Example 7-2. At constant absolute pressure of 2 bar and temperature of 288 K 2 kg of air expands to final temperature of 423 K. Determine the final volume of the air, the amount of heat added and the work of expansion done.

Answer. $V_2=2.54$ m^3; $Q_{exp}=277$ kJ; $L=79.2$ kJ.

Example 7-3. 12 kg of air kept at an absolute pressure of 6 bar and temperature of 300 K expands at constant temperature until the volume of the air increases four times. Determine the initial and final parameters of the air, the amount of heat added and the work of expansion performed.

The initial volume of the air is determined from the equation of state

$$V_1=\frac{mRT_1}{p_1}=\frac{12\times287.04\times300}{6\times10^5}=1.725 \text{ m}^3.$$

The final volume

$$V_2=1.725\times4=6.9 \text{ m}^3.$$

The final pressure is equal to

$$p_2=\frac{p_1V_1}{V_2}=\frac{6\times1.725}{6.9}=1.5 \text{ bar}.$$

The work of expansion

$$L=p_1V_1 \ln V_2/V_1=2.303\times6\times10^5\times1.725 \log 6.9/1.725=$$

$$=1\,450\,000 \text{ J}=1450 \text{ kJ}.$$

The amount of added heat is equal to the work of expansion

$$Q=L=1450 \text{ kJ}.$$

Example 7-4. At an initial absolute pressure of 10 bar and temperature of 600 K 2 kg of air expands adiabatically to a pressure of 1 bar. Determine the final volume, final temperature and the work of expansion. The adiabatic exponent for a diatomic gas $k=1.4$.

The initial volume of air is determined from the equation of state

$$V_1=\frac{mRT_1}{p_1}=\frac{2\times287.04\times600}{10\times10^5}=0.345 \text{ m}^3.$$

From the equation of an adiabat we obtain

$$V_2=V_1(p_1/p_2)^{1/k}=0.345(10/1)^{1/1.4}=1.79 \text{ m}^3.$$

The final temperature is determined by formulea

$$T_2=\frac{p_2V_2}{mR}=\frac{1\times10^5\times1.79}{2\times287.04}=312 \text{ K}$$

The work of expansion is equal to

$$L=[1/(k-1)](p_1V_1-p_2V_2)=[10^5/(1.4-1)](10\times0.345-1\times1.79)=$$
$$=415\,000 \text{ J}=415 \text{ kJ}.$$

Example 7-5. 3 kg of air kept at initial parameters of $p_1=1$ bar and $T_1=300$ K is polytropically compressed to a pressure $p_2=15$ bar, and air temperature rises to $T_2=500$ K.

Determine the polytropic exponent, the final volume, the work of compression and the amount of heat rejected from the air.

The polytropic exponent

$$(n-1)/n=\frac{\log T_2/T_1}{\log p_2/p_1}=\frac{\log 500/300}{\log 15/1}=0.187,$$

whence $n=1.23$.

The final volume

$$V_2=\frac{mRT_2}{p_2}=\frac{3\times287.04\times500}{15\times10^5}=0.287 \text{ m}^3.$$

The initial volume

$$V_1=V_2(p_2/p_1)^{1/n}=0.287(15/1)^{1/1.23}=2.57 \text{ m}^3.$$

The work of compression

$$L=[1/(n-1)](p_1V_1-p_2V_2)=[10^5/(1.23-1)](1\times2.57-15\times0.287)=$$
$$=-763\,000 \text{ J}=-763 \text{ kJ}.$$

The amount of heat rejected

$$Q=mc_v[(n-k)/(n-1)](T_2-T_1)=3\times0.72[(1.23-1.4)/(1.23-1)](500-$$
$$-300)=-316 \text{ kJ},$$

where

$$c_v=\mu c_v/\mu=20.8/28.9=0.72 \text{ kJ/kg·deg}.$$

The change in external energy

$$\Delta u=mc_v(T_2-T_1)=3\times0.72\times200=432 \text{ kJ}.$$

When air is compressed polytropically with an exponent $n=1.23$ the work of compression is divided into two fractions: one fraction is transferred in the form of heat to a low-temperature source (refrigerator); the other fraction of work is expended to increase the internal energy of the working medium.

Example 7-6. The temperature of air undergoing a polytropic process changes from 120 to 50 °C. The initial air pressure $p_1=5$ bar. Determine the change of the entropy of air, if 60 kJ/kg of heat is transferred to the air during the processes. The heat capacity of air (see example 7-5) $c_v=0.72$ kJ/kg·deg.

The polytropic exponent is determined from equation

$$q=c_v[(n-k)/(n-1)](t_2-t_1),$$

whence

$$(n-1.4)/(n-1)=q/c_v(t_2-t_1)=60/0.72(50-120)=-1.19, \text{ and } n=1.18.$$

The final pressure p_2 is determined from

$$p_2/p_1=(T_2/T_1)^{n/(n-1)}, \quad p_2=p_1(T_2/T_1)^{n/(n-1)}=5(323/393)^{6.56}=1.38 \text{ bar.}$$

The change of entropy is

$$s_2-s_1=c_p \ln T_2/T_1-R \ln p_2/p_1=1.0\times 2.3 \log 0.822-$$
$$-0.287\times 2.3 \log 0.276=0.173 \text{ kJ/kg·deg.}$$

The change of entropy can also be found from another formula

$$s_2-s_1=c_v\frac{n-k}{n-1}\ln\frac{T_2}{T_1}=0.173 \text{ kJ/kg·deg.}$$

CHAPTER EIGHT

THE SECOND LAW OF THERMODYNAMICS

8-1. The Fundamentals of the Second Law of Thermodynamics

Being a special case of the general law of conservation and conversion of energy, the first law of thermodynamics states that heat can be converted into work, and work into heat, but it does not state the conditions under which these conversions are possible.

The law fails to consider the direction of the thermal process and not knowing this direction it is impossible to foretell the nature of the process and its results.

For instance, the first law of thermodynamics does not determine whether heat will be transferred from a body at a higher temperature to a body at a lower temperature or vice versa. Everyday observations and experiments show that spontaneous heat flow is possible only from bodies at a higher temperature to bodies at a lower temperature. Heat transfer from a body at a higher temperature to a medium will continue until complete temperature equilibrium sets in between the body and the surrounding medium. The direction of heat flow can only be changed at the expense of work.

This property of heat distinguishes it essentially from work.

Just as any other kinds of energy taking part in a process, work converts easily and completely into heat. The complete convertibility of work into heat was known to man in ancient times, when he struck fire by rubbing two pieces of wood. Processes involving conversion of work into heat occur in nature continuously, some examples being friction, impact, braking, etc.

For instance, the behaviour of heat is quite different in heat engines. There, heat is converted into work only when there is a temperature difference between the source of heat and the medium to which heat is transferred (heat sink or low-temperature source). In this process of conversion all the heat cannot be converted into work.

It follows from the foregoing that a profound difference exists between the conversion of heat into work and vice versa. The law that indicates the direction of heat flow and establishes a maximum limut up to which the conversion of heat into work is possible in heat engines is a new law, established experimentally. This is the *second law of thermodynamics* which is important for all thermal processes. The second law of thermodynamics is not confined to engineering, it is used in physics, chemistry, biology, astronomy, etc.

In 1824, a French engineer and scientist, Sadi Carnot, reasoning on the

motive power* of fire outlined the essence of the second law of thermodynamics. He wrote: "Wherever a temperature difference exists a motive power may appear. The motive power of heat does not depend on the agents taken for its development: its amount is determined only by the temperature of the bodies between which, in the final analysis, caloric, or phlogiston, is transferred. The initial temperature of gas must be as high as possible, to ensure a considerable development of the motive power. For the same reason the cooling should be as great as possible. It cannot be hoped that it will ever be possible to make practical use of the entire motive power of fuel."

In the fifties of the last century Ch. Clausius proposed the most general and modern formulation of the second law of thermodynamics stating that "heat cannot pass on its own from a body of lower temperature to a body of higher temperature (without compensation)". The Clausius postulate should be considered as an experimental law obtained from the observation of nature. Clausius' statement was made and applied to engineering, but it happened that the second law was also true for physical and chemical phenomena. Just as all other formulations of the second law of thermodynamics, the Clausius statement expressed one of the main, but not absolute laws of nature, since it was formulated as applied to objects of finite dimensions in the earthy conditions surrounding us.

In 1851, simultaneously with Clausius, W. Thomson suggested another statement of the second law of thermodynamics from which it follows that not all the heat transferred from a hot body but only a fraction of it can be converted into work. A fraction of the heat must pass into a low-temperature source or heat sink.

Consequently, to obtain work there must exist a *high-temperature heat source* or *hot body* and a low-temperature source or *heat sink*. In addition, Thomson's statement of the second law of thermodynamics shows that it is impossible to build a perpetual motion machine which would perform work only at the expense of the internal energy of seas, oceans and air. This statement can be formulated as the second law of thermodynamics: "it is impossible to build a perpetual motion machine of the second kind" (W. Ostwald).

By a perpetual motion machine of the second kind is meant a machine able to convert into work all the heat received only from one source.

In addition to the one outlined above, there exist several more statements of the second law of thermodynamics which, in essence, do not introduce anything new and are, therefore, not mentioned here.

* By "motive power" Carnot meant work.

8-2. Cyclic Thermodynamic Processes, or Cycles

In the thermodynamic processes considered above we studied problems involving the performance of work either due to added heat or due to a change in the internal energy of the working medium, or simultaneously as a result of heat transfer and a change of internal energy. Upon single expansion of a gas in a cylinder it is possible to obtain but a restricted amount of work. In fact, in any process involving the expansion of a gas in a cylinder, the moment sets in when the temperature and the pressure of the working medium become equal to the temperature and pressure of the surrounds, and then the performance of work ceases.

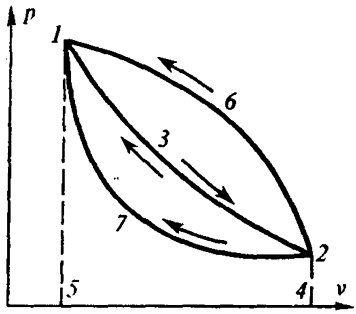


FIG. 8-1

Consequently, to reobtain work, in the course of compression, the working medium must be returned into its initial state. It follows from Fig. 8-1 that if the working medium expands along the curve *1-3-2*, it produces work represented on the *p-v* diagram by area *13245*. When point *2* is attained the working medium must be returned into its initial state (into point *1*) so as to enable the working medium to produce work again. The working medium can be returned into the initial state in three ways.

1. The compression curve *2-3-1* coincides with the expansion curve *1-3-2*. In this process all the work obtained as a result of expansion (area *13245*) is equal to the work of compression (area *23154*) and the positive work is equal to zero.

2. The curve of compression *2-6-1* runs on top of the line of expansion *1-3-2;* more work (area *51624*) is then expended to realize compression than the amount of work obtained upon expansion (area *51324*).

3. The curve of compression *2-7-1* lies below the line of expansion *(1-3-2)*. This cyclic process is characterized by the fact that the work of expansion (area *51324*) is greater than the work of compression (area *51724*). As a result positive work will be transferred to the outside, represented by area *13271* inside the closed line of the cyclic process, or cycle.

Repeating the cycle an unlimited number of times, the heat added can be used to produce any amount of work.

A cycle resulting in the performance of positive work is referred to as a *direct,* or *forward, cycle* or the *cycle of heat engine;* the work of expansion is greater than the work of compression. The cycle involving the expenditure of work is said to be a *reverse* cycle; the work of compression in this cycle is greater than the work of expansion. The reverse cycles are the operating cycles of refrigerating machines.

There are reversible and irreversible cycles. A cycle consisting of equilibrium reversible processes is called a *reversible* cycle. The working medium in this cycle should not undergo any chemical transformations.

Even if one of the component processes of a cycle is an irreversible one, the entire cycle shall be *irreversible.*

The results obtained in the investigation of ideal cycles can be applied to real, irreversible processes occurring in real machines by the introduction of empirical correction factors.

8-3. Thermal Efficiency and Refrigerating Factor of Cycles

A study of any reversible cycle makes it clear that in order to realize it, it is necessary that at any point of the forward process heat must be transferred from high-temperature heat sources to the working medium at an infinitely small temperature difference and removed from the working medium to sources also at an infinitely small temperature difference; as this takes place there should be infinitely small difference between the temperatures of two neighbouring heat sources, since, otherwise, at a finite temperature difference the heat-transfer processes shall be irreversible. Hence, to create the heat engine, it is necessary to have a great number of high-temperature and low-temperature heat sources and a working medium.

Along the path *1-3-2* (Fig. 8-1) the working medium produces work of expansion l_1, equal numerically to area *513245*, at the expense of heat q_1, transferred from the sources and, partly, at the expense of its own internal energy. Along the path *2-7-1* the work of compression l_2 is expended, equal numerically to area *427154*, a fraction of which, converted into heat q_2, is transferred, or rejected, to the sinks, and the other fraction is spent to increase the internal energy of the working medium to its initial value. The realization of a forward cycle results in the transfer of positive work to the outside, its amount being equal to the difference between the works of expansion and compression. This work $l=l_1-l_2$.

The amounts of heat q_1 and q_2 and the positive work l are interrelated by the first law of thermodynamics

$$q=q_1-q_2=u_2-u_1+l.$$

Since in the cycle the final state of the working medium coincides with the initial state, the internal energy of the working medium does not change and is equal to zero, therefore $q_1-q_2=l$.

The ratio of the quantity of heat converted into positive work in one cycle to the entire amount of heat added to the working medium is referred to as the *thermal efficiency* of a forward cycle

$$\eta_t=(q_1-q_2)/q_1=1-q_2/q_1=l/q_1. \qquad (8\text{-}1)$$

The magnitude of η_t indicates the degree of perfection of the cycle of a heat engine. The greater η_t the larger the fraction of the heat added that is converted into useful work. The thermal efficiency of a cycle is always less

than unity and could be equal to unity, if $q_1 \to \infty$ or $q_2 = 0$ which cannot be realized.

Equation (8-1) shows that all the heat added to the working medium in the cycle, q_1, cannot be fully converted into work without rejecting a certain amount of heat q_2 to a sink.

Thus, the main idea of Carnot proved to be true, namely: in a closed cyclic process heat can be converted into mechanical work only in the presence of difference between the temperatures of the high-temperature and low-temperature heat sources. The greater this difference the higher the cycle efficiency of a heat engine.

Let us consider now a reverse cycle that proceeds counterclockwise and is depicted on a *p-v* diagram by area *13261* (Fig. 8-1). In this cycle the working medium expands at a temperature that is lower than the compression temperature and the work of expansion (area *132451*) is smaller than the work of compression (area *162451*). Such a cycle can only be realized at the expense of external work.

In a reverse cycle the amount of heat q_2 is transferred from the sink to the working medium and the work l spent is converted into an equal amount of heat that is transferred together with heat q_2 to the source

$$q_1 = q_2 + l.$$

Heat transfer of this kind is impossible on its own without the expenditure of work. The degree of perfection of a reverse cycle is determined by the so-called *refrigerating factor of the cycle*

$$\varepsilon = \frac{q_2}{l}.$$

The refrigerating factor, or coefficient of performance, indicates the quantity of heat transferred from a high-temperature source upon the expenditure of unit work. As a rule, the refrigerating factor is greater than unity.

8-4. Forward Reversible Carnot Cycle

When an arbitrary reversible cycle is realized the number of heat sources can be reduced, if on individual sections of the cycle heat will be transferred to and from the working medium at a constant temperature, i.e. in isothermal processes. The limiting case is that when all the heat involved in the cycle is transferred to and from the working medium in isothermal processes. Only two constant-temperature heat sources are required a limiting case of this kind: one source and one sink.

A reversible cycle can be realized in these conditions in the following way. First, in an isothermal process of expansion, heat is transferred reversibly to the working medium from a source. Then, in a reversible adiabatic process of expansion, in the course of which there is no heat exchange between the working medium and the heat sources, the tempera-

ture of the working medium is lowered to that of the low-temperature source. After that, in a reversible isothermal process, at the temperature of the sink heat is transferred from the working medium to that source. The cycle must be closed with a reversible adiabatic process in the course of which, in the absence of heat exchange with external heat sources, temperature is raised to the initial one and the working medium returns to its initial state. Thus, a reversible cycle realized between two constant-temperature heat sources must consist of two reversible isothermal and two reversible adiabatic processes.

This cycle was first considered by Sadi Carnot in his work "Reflexions sur la puissance motive the feu" published in 1824. This cycle is depicted on the p-v diagram shown in Fig. 8-2.

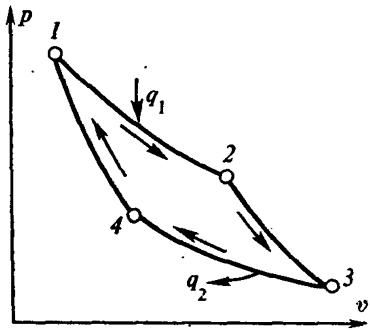


FIG. 8-2

For a better understanding of the way in which this cycle is realized let us imagine a heat engine whose cylinder can serve both as an absolute heat conductor and an absolute heat insulator as needed. When the piston is in the first position let the initial parameters of the working medium be p_1, v_1, and let temperature T_1 be equal to the temperature of the high-temperature source. If at that moment the cylinder is an absolute heat conductor and it is brought into contact with a source of infinitely-large heat capacity, transferring to the working medium heat q_1 along isotherm *1-2*, the gaseous working medium shall expand to point *2* and produce work. The parameters of point *2* are p_2, v_2, T_1. From point *2* the cylinder must cease an absolute heat insulator. The working medium at the temperature T_1, expanding adiabatically along line *2-3* to the temperature of the sink, performs work. The parameters of point *3* are p_3, v_3, T_2. From point *3* let us make the cylinder an absolute heat insulator. Compressing the working medium along isotherm *3-4*, we transfer simultaneously heat q_2 to the sink. At the end of the isothermal compression the parameters of the working medium shall be p_4, v_4, T_2. From point *4* in an absolute non-heat insulator cylinder the working medium undergoes adiabatic process of compression and returns to its initial state.

Thus, in the course of the entire cycle heat q_1 was added to the working medium from the high-temperature source and heat q_2 was transferred (rejected) from the working medium to the sink. The thermal efficiency of the cycle

$$\eta_t = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1}.$$

The heat added to the working medium along isotherm *1-2* is

$$q_1 = RT_1 \ln v_2/v_1.$$

The absolute value of the heat rejected in the cycle along isotherm *3-4* is found to be equal to

$$|q_2| = RT_2 \ln v_3/v_4.$$

Substituting the found values of q_1 and q_2 into the equation for thermal efficiency, we obtain

$$\eta_t = 1 - \frac{RT_2 \ln \frac{v_3}{v_4}}{RT_1 \ln \frac{v_2}{v_1}} = 1 - \frac{T_2 \ln \frac{v_3}{v_4}}{T_1 \ln \frac{v_2}{v_1}}.$$

For the process of adiabatic expansion and compression respectively we have

$$\left(\frac{T_2}{T_1}\right)^{1/(k-1)} = \frac{v_2}{v_3} \quad \text{and} \quad \left(\frac{T_2}{T_1}\right)^{1/(k-1)} = \frac{v_1}{v_4}$$

whence

$$\frac{v_2}{v_3} = \frac{v_1}{v_4} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{v_3}{v_4}.$$

Consequently, after cancelling, the equation of thermal efficiency of a Carnot cycle acquires the following appearance

$$\eta_t = 1 - T_2/T_1. \tag{8-2}$$

The thermal efficiency of a reversible Carnot cycle depends only on the absolute temperature of the source and the sink. The thermal efficiency will be higher, the higher the temperature of the source and the lower the temperature of the sink. The thermal efficiency of a Carnot cycle is always less than unity, since for the thermal efficiency to be greater than unity the temperature T_2 must be equal to zero or $T_1 = \infty$, which cannot be realized. The thermal efficiency of a Carnot cycle is independent of the nature of the working medium and is equal to zero at $T_2 = T_1$, i.e. when the system is in thermal equilibrium heat cannot be converted into work.

The thermal efficiency of a Carnot cycle is greater than that of any other cycle realized in the same temperature interval (see Sec. 8-15). Therefore, a comparison of the thermal efficiences of any cycle and the Carnot cycle permits a conclusion on the degree of perfection with which heat is utilized in the machine operated on the given cycle.

In real engines the Carnot cycle is not realized due to the practical difficulties involved. However, the theoretical and practical importance of the Carnot cycle is rather great. It serves as a reference when evaluating the degree of perfection of any cycle realized in heat engines. A reversible Carnot cycle realized in the temperature interval T_1 and T_2 is represented on a *T-s* diagram by the rectangle *1234* (Fig. 8-3).

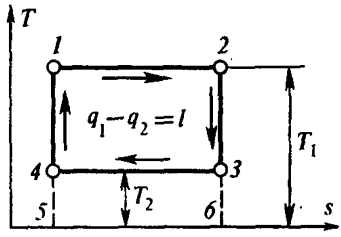


FIG. 8-3

8-5. The Reverse Reversible Carnot Cycle

The carnot cycle can proceed not only in the direct, or forward, but also in the reverse direction. A reverse Carnot cycle is represented in Fig. 8-4. The cycle is composed of reversible processes and is reversible as a whole.

From the initial point *1* the working medium expands along the adiabat *1-4* without heat transfer to and from the surrounding medium, and the temperature drops from T_1 to T_2. Then, along the isothermal line *4-3* the gas continues to expand with the addition of heat q_2 transferred from a heat sink at a temperature T_2. Further the working medium is compressed adiabatically along line *3-2* causing a rise in the temperature of the working medium from T_1 to T_2. The final process of the cycle involves isothermal compression of the working medium along line *2-1* in the course of which heat q_1 is transferred to the low-temperature source.

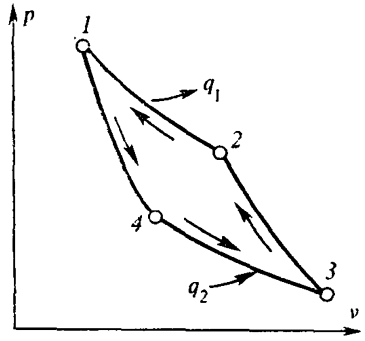


FIG. 8-4

Considering the reverse cycle as a whole, it will be noted that the expended external work of compression is greater than the work of expansion by the magnitude of area *14321* inside the closed line of the cycle. This work converts into heat and is transferred together with the heat q_2 to the heat source at the temperature T_1. Thus, work l is spent to realize the reverse cycle, and it is possible to transfer from the sink to the source q_2 units of heat, with the heat transferred to the low temperature source being equal to

$$q_1 = q_2 + l.$$

A machine operated on the reverse cycle is called a *refrigerating machine.*

Considering the reverse Carnot cycle, we can come to the conclusion that, in accordance with Clausius statement of the second law of thermodynamics, heat cannot be transferred spontaneously, without the expenditure of energy, from a sink to a source (a compensation is necessary for the heat-transfer process to take place).

The efficiency of refrigerating machines is characterized by the refrigeration factor or coefficient of performance

$$\varepsilon = q_2/(q_1 - q_2) = q_2/l, \tag{8-3}$$

or for a reverse Carnot cycle

$$\varepsilon = T_2/(T_1 - T_2). \tag{8-4}$$

The refrigeration factor of the reverse Carnot cycle depends on the absolute temperatures T_2 and T_1 of the heat sources and it exceeds the

refrigeration factors of other cycles occurring in the same temperature interval.

Having considered the direct, or forward, and reverse Carnot cycles, it is now possible to investigate in greater detail the formulation of the second law of thermodynamics suggested by Ch. Clausius.

Clausius has shown that all natural processes are spontaneous processes (they are sometimes referred to as positive, or non-compensated, processes) and they cannot "by themselves", without compensation, occur in the reverse direction.

Spontaneous processes include: the flow of heat from a body at a higher temperature to a body at a lower temperature; conversion of work into heat; mutual diffusion of fluids (liquids and gases); expansion of a gas into a vacuum (evacuated space), etc.

Non-spontaneous processes include processes of a reverse nature, such as the process of heat flow from a body of lower temperature to a body of higher temperature, conversion of heat into work; separation of mutually diffused substances into components, etc. Non-spontaneous processes are possible, but they never proceed "by themselves", without compensation. When non-spontaneous processes involve the conversion of heat into work, then simultaneously with cooling of the high-temperature source, a change of the thermodynamic state of one or several bodies also takes place. In thermodynamics, this change is called the *compensation for the conversion of heat into work*. Let us consider a few examples.

When an ideal gas undergoes isothermal expansion its internal energy does not change, and all the heat added to the gas converts into work. The conversion of heat into work is compensated for by the spontaneous process of gas expansion. If, without a change in the temperature, the gas is to be returned into its initial state, it would be necessary to expend the same amount of work to compress the gas with the same quantity of heat being released. Ultimately, no conversion of heat into work would take place.

What are the processes that must accompany non-spontaneous processes, to make them feasible? A thorough and comprehensive study of the physical phenomena surrounding us has shown that non-spontaneous processes are possible only when they are accompanied by spontaneous processes. Consequently, a spontaneous process can proceed "by itself", and a non-spontaneous process—only together with spontaneous ones. This means that spontaneous processes of natural conversion of work into heat occur "by themselves", and non-spontaneous processes of converting heat into work cannot be realized without compensation. That is why, for instance, in any forward cyclic process the non-spontaneous process of conversion of heat into work is compensated for by the simultaneously occurring spontaneous process involving the transfer of a fraction of the heat added from a source to a sink ($l=q_1-q_2$).

When a reverse cycle is realized non-spontaneous transfer of heat from a body at a lower temperature to a body at a higher temperature is also

possible, but here this process is compensated for by the spontaneous conversion of external work into heat ($q_1=q_2+l$).

Thus, any non-spontaneous process may only occur when it is accompanied by a compensating spontaneous process.

8-6. The Carnot Theorem

In deriving the thermodynamic efficiency of the reversible Carnot cycle, use was made of relationships which are true only for an ideal gas. Therefore, to apply all that has been said above about the Carnot cycle to any real gases and vapours, it must be proved that the thermal efficiency of the Carnot cycle does not depend on the properties of the substance used to realize the cycle. This is the content of the Carnot theorem.

To prove this theorem, let us assume that two engines operate on a reversible Carnot cycle with different working media (Fig. 8-5). The working

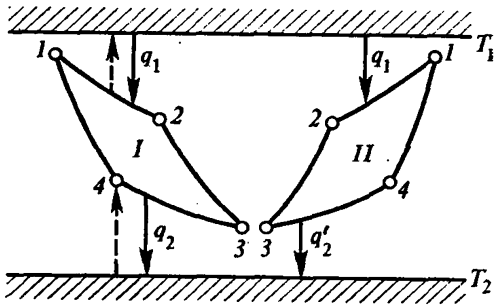


FIG. 8-5

medium in the first engine *I* is an ideal gas, and that of the second engine *II*—is vapour (steam). The two engines have a common source and a common sink. Let a quantity of heat q_1 be transferred to the working media in the gas and steam engines, and let an amount of heat q_2 be rejected from the gas machine and q_2'—from the steam engine to the heat sink. The efficiency of these engines

$$\eta_t=(q_1-q_2)/q_1 \quad \text{and} \quad \eta_t'=(q_1-q_2')/q_1.$$

The two efficiencies shall be equal if $q_2=q_2'$, and different if $q_2\neq q_2'$.

The Carnot theorem is proved by contradiction. Let us assume that $q_2'<q_2$, then $\eta_t'>\eta_t$, i.e. the steam engine performs a large amount of positive work. Let us prove that this is impossible. Let us mount the two engines on a common shaft and have the steam engine operate on the forward cycle *1-2-3-4-1*, and the gas engine—on the reverse cycle *1-4-3-2-1*. The steam engine receives heat q_1, and rejects heat q_2'. The positive work l' of the cycle is presented by area *12341* and is equal $l'=q_1-q_2'$.

The gas engine realizes a reverse Carnot cycle. Heat q_2 is transferred to the working medium of the gas machine from a sink, and the machine

expends work l. Upon completion of the cycle, the heat source receives heat q_1. The expended work is equal to $l=q_1-q_2$.

Taking into account the assumed condition that $q_2'<q_2$, the performance of the two machines results in the availability of excess work

$$l'-l=(q_1-q_2')-(q_1-q_2)=q_2-q_2'>0.$$

Operation of the two machines caused the following changes: the amount of heat q_1 was transferred from and to the source; the amount of heat q_2 was transferred from the sink, and q_2' was transferred to it, resulting in a net loss of q_2-q_2' which was spent to perform positive work, with no changes taking place in the system and the surrounding medium.

Thus, a perpetuum mobile of the IInd kind was obtained, and this contradicts the second law of thermodynamics. Thus, the assumption that $q_2'<q_2$ is erroneous.

The same result is obtained if we assume that $q_2'>q_2$. Therefore, one possible alternative is left when $q_2'=q_2$, and this means that the thermal efficiency η_t' is also equal to η_t, i.e. in fact, the thermal efficiency of the reversible Carnot cycle does not depend on the properties of the working medium and is only a function of the temperatures of the high- and low-temperature sources.

8-7. Properties of Reversible and Irreversible Cycles and the Mathematical Statement of the Second Law of Thermodynamics

It follows from the expression for thermal efficiency that

$$\eta_t=1-Q_2/Q_1,$$

but thermal efficiency for the reversible Carnot cycle is also expressed in terms of the temperatures of the heat sources, namely

$$\eta_t=1-T_2/T_1.$$

Comparing the two equations, it is clear that for the Carnot cycle

$$\frac{Q_2}{Q_1}=\frac{T_2}{T_1} \quad \text{and} \quad \frac{Q_1}{T_1}=\frac{Q_2}{T_2} \quad \text{or} \quad \frac{Q_1}{T_1}-\frac{Q_2}{T_2}=0.$$

Let us assume the added heat Q_1 to be positive and the rejected heat Q_2—negative, then

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}=0 \quad \text{or} \quad \Sigma\frac{Q}{T}=0. \tag{8-5}$$

The ratio of the added or rejected heat to the corresponding absolute temperature is referred to as the *reduced heat*. Then, the equality (8-5) can be formulated as follows: for the reversible Carnot cycle the algebraic sum of the reduced heats is equal to zero.

This conclusion can also be applied to any arbitrary reversible cycle.

Let us consider some arbitrary reversible cycle *1-2-3-4-1* (Fig. 8-6). Let us divide such a cycle into an infinitely large number of elementary cycles with the aid of adiabatic lines. Each elementary cycle can be assumed to be an elementary Carnot cycle. The infinitely small sections along which heat is added and rejected can be assumed to be isotherms and the adiabats do not influence the magnitude of useful work, since each of them passes two times in opposite directions.

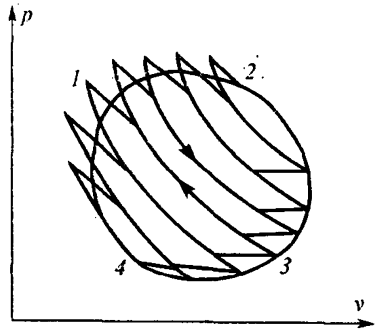


FIG. 8-6

For each elementary Carnot cycle

$$\Sigma dQ/T=0,$$

and for the entire arbitrary cycle

$$\oint dQ/T=0. \qquad (8\text{-}6)$$

The sign $\oint$ indicates integration over a closed contour.

Thus, for any reversible cycle the algebraic sum of the reduced heats is equal to zero.

Derived by Ch. Clausius in 1854, Eq. (8-6) is the mathematical expression of the second law of thermodynamics for an arbitrary reversible cycle, and is called the *first Clausius integral.*

For the same temperatures of the source and the sink, the thermal efficiency of an irreversible Carnot cycle is smaller than the corresponding efficiency of a reversible cycle

$$\eta_{t\,ir}<\eta_{t\,rev}$$

or

$$1-Q_2/Q_1<1-T_2/T_1;$$

$$T_2/T_1<Q_2/Q_1; \quad Q_1/T_1<Q_2/T_2 \quad \text{and} \quad Q_1/T_1-Q_2/T_2<0.$$

Since the ratio Q_2/T_2 is negative, then for an irreversible Carnot cycle we obtain

$$\frac{Q_1}{T_1}-\left(-\frac{Q_2}{T_2}\right)<0, \quad \text{or} \quad \Sigma\frac{Q}{T}<0.$$

For an irreversible Carnot cycle the algebraic sum of the reduced heats is less than zero; it is a negative quantity. For an arbitrary irreversible cycle, composed of an infinitely large number of irreversible elementary cycles, we obtain

$$\oint dQ/T<0. \qquad (8\text{-}7)$$

The inequality (8-7) is the mathematical expression of the second law

of thermodynamics for an arbitrary irreversible cycle and it is called the *second Clausius integral* or the *Clausius inequality.*

Combining the two formulae (8-6) and (8-7), the second law of thermodynamics can be expressed by a single equation

$$\oint dQ/T \leqslant 0, \tag{8-8}$$

where the equality sign pertains to reversible and the inequality sign—to irreversible cycles.

8-8. Change of Entropy in Reversible and Irreversible Processes

In a reversible cyclic process the integral of dQ/t taken over a closed circuit is equal to zero. Therefore, the quantity dQ/T is the total differential of some function depending only on the given state of a body. This function is denoted by S and is called the *entropy*. Then,

$$dS = dQ/T. \tag{8-9}$$

Upon integration of Eq. (8-9) over any path *1-2*, we obtain

$$S_2 - S_1 = \int_1^2 dQ/T. \tag{8-10}$$

For a reversible adiabatic process, when $dQ=0$,

$$dS=0 \quad \text{and} \quad S_2 = S_1 = \text{const},$$

i.e. in an adiabatic reversible process entropy does not change.

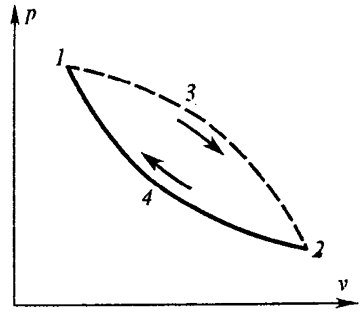


FIG. 8-7

Let us consider the change of entropy in irreversible processes. For this purpose let us draw between states *1* and *2* the reversible process *2-4-1* and trace arbitrarily with a dotted line the irreversible process *1-3-2* (Fig. 8-7). The cycle composed of these processes shall be an irreversible one. According to Eq. (8-7) we obtain

$$\int_{1\text{-}2\text{-}3} dQ/T + \int_{2\text{-}4\text{-}1} dQ/T < 0.$$

Since the process *2-4-1* is reversible, the second integral is equal to the difference $S_1 - S_2$, therefore

$$\int_{1\text{-}3\text{-}2} dQ/T + (S_1 - S_2) < 0,$$

or

$$S_2 - S_1 < \int_{1\text{-}2\text{-}3} dQ/T. \tag{8-11}$$

The inequality sign in Eq. (8-11) indicates that in the event of an irreversible process the integral in the right-hand side of the equation no longer expresses the entropy difference, but is less than it. Combining Eqs. (8-10) and (8-11), we find

$$S_2 - S_1 \geqslant \int_1^2 dQ/T. \tag{8-12}$$

Entropy is a function of state, therefore the change of entropy shall be the same both for reversible and irreversible processes. Equation (8-12) indicates that for a reversible process the integral $\int_1^2 dQ/T$ equals the change of entropy $S_2 - S_1$, and for an irreversible process it is less than $S_2 - S_1$.

Since Eq. (8-8) expresses the second law of thermodynamics, then Eq. (8-12) expresses the same law, but for a more general case. Expression (8-8) is only applicable to cycles, whereas expression (8-12) can be applied to any processes in which the initial and final states *1* and *2* differ. Expression (8-8) is derived as a special case of expression (8-12).

For an elementary irreversible process

$$ds > dQ/T. \tag{8-13}$$

Combining Eqs. (8-9) and (8-13), we can write that for any process the change of entropy satisfies the following relationship

$$ds \geqslant dQ/T, \tag{8-14}$$

where dQ = the amount of heat transferred to the body from the heat source;

T = absolute temperature of the heat source; the equality sign pertains to reversible, and the sign "greater than"—to irreversible processes.

All the above formulae and, in particular, Eq. (8-12) permit determination only of the change of entropy.

The value of entropy for any given state must always contain some constant value S_0 (integration constant) that represents the magnitude of the entropy of a body at absolute zero temperature

$$S = \int dQ/T + S_0,$$

where the integral is taken along an arbitrary reversible process. The numerical value of the integration constant S_0 cannot be determined with

the aid of the first and second laws of thermodynamics. It will be shown below that this quantity is determined with the help of the so-called Nernst heat theorem (see Sec. 9-10).

For many practical thermodynamic problems it is not the absolute magnitude of entropy, but its change which is important, and this makes the numerical value of the integration constant S_0 immaterial. The value of S_0 is usually selected arbitrarily, depending upon conditions of practical convenience.

8-9. Generalized (Regenerative) Carnot Cycle

In a given temperature interval it is impossible to realize a cycle with a thermal efficiency exceeding that of a reversible Carnot cycle. However, in the presence of two constant-temperature heat sources, it is possible to realize other reversible cycles differing in configuration from the Carnot cycle, but having in some supplementary conditions the thermal efficiency, equal to that of the Carnot cycle. Such cycles are referred to as generalized or regenerative.

The cycle *1-2-3-4* shown in Fig. 8-8 consists of two isotherms *1-2* and *3-4* and any two arbitrary processes *2-3* and *4-1* that are equidistant in the horizontal direction. In the isothermal process *1-2* heat is transferred from a source at temperature T_1 to the working medium, its amount being $q_1=T_1(s_2-s_1)$. In the process *2-3* the working medium changes its state and rejects a certain amount of heat $q_{2\text{-}3}$, represented on the diagram by area *7328*. For the reversible process *2-3* to be realized, during which the working medium changes its temperature from T_1 to T_2, an infinitely great number of intermediate heat sources must be available their temperatures differing from one another by an infinitely small quantity. From point *3* to point *4* the working medium undergoes isothermal compression rejecting an amount of heat $q_2=T_2(s_3-s_4)$ to the sink at the temperature T_2, then the working medium returns to the state at point *1* along the line *4-1*. As it passes from point *4* to point *1*, the working medium absorbs heat $q_{4\text{-}1}$, measured by area *5416*. When the reverse process *4-1* is realized the same intermediate heat sources that served as sinks in the process *2-3* are used as sources now. Due to the fact that the processes *2-3* and *4-1* are equidistant the areas *7328* and *5416* are equal to each other and the amounts of heat $q_{2\text{-}3}$ and $q_{4\text{-}1}$ are equal numerically, i.e. the amount of heat that the working medium rejects in the process *2-3* is equal to the amount of heat that is added to it in the process *4-1*. All these intermediate sinks and sources are merely heat regenerators to which heat is transferred from the working medium on one section of the cycle and from which the same amount of

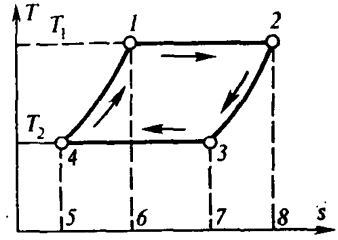


FIG. 8-8

heat is transferred to the working medium on the other section of the cycle. In the cycle *1-2-3-4*, only the source at the temperature T_1 and the sink at the temperature T_2 serve as actual external heat sources. The work output of the cycle is obtained at the expense of heat q_1 that is transferred from the source to the working medium; another, equal to q_2, is transferred to the sink, and the difference between these amounts of heat, q_1-q_2, is converted into the positive work output of the cycle.

Indeed,

$$l=q_1-q_{2\text{-}3}-q_2+q_{4\text{-}1},$$

or

$$l=q_1-q_2.$$

The thermal efficiency of this cycle is determined by the equation

$$\eta_t=\frac{q_1-q_2}{q_1}=\frac{T_1(s_2-s_1)-T_2(s_3-s_4)}{T_1(s_2-s_1)}.$$

Since the curves *2-3* and *4-1* are equidistant, then

$$s_1-s_4=s_2-s_3 \quad \text{and} \quad s_2-s_1=s_3-s_4$$

and the efficiency of the cycle is

$$\eta_t=(T_1-T_2)/T_1.$$

The thermal efficiency of the reversible cycle considered is equal to the thermal efficiency of the reversible Carnot cycle.

A cycle in which heat regenerators are involved is called a *regenerative cycle.* A regenerative reversible cycle consisting of two isotherms and any two arbitrary equidistant curves is referred to as the *generalized* (regenerative) Carnot cycle. Regenerative cycles have found wide application in heat power plants.

8-10. The Principle of Entropy Increase and the Physical Meaning of the Second Law of Thermodynamics

Let us consider the change of entropy in an isolated, closed, system that does not exchange heat with the surrounding medium ($dQ=0$); the system can be called an *adiabatic system.*

Let us assume that there exists an isolated adiabatic system in which thermodynamic processes occur. If only reversible processes develop in that isolated system, then applicable to it is Eq. (8-9)

$$dS=dQ/T,$$

but for an adiabatic system this equation acquires the appearance

$$dQ=T\,dS=0.$$

Since temperature cannot be equal to zero, for the entire system

$$dS=0 \quad \text{and} \quad S=\text{const.} \tag{8-15}$$

If only reversible processes proceed in the isolated adiabatic system, then the entropy of the entire system remains constant.

Let us consider an adiabatic system undergoing an irreversible processes to which Eq. (8-13) is applicable

$$dS>dQ/T$$

Since $dQ=0$, then for the isolated adiabatic system

$$dS>0, \tag{8-16}$$

i.e. an increase of entropy takes place.

Thus, Eqs. (8-15) and (8-16) indicate that the entropy of isolated systems can remain constant ($dQ=0$) if it changes reversibly and increase in the event of irreversible changes, but under no circumstances can entropy decrease. It should be noted that the entropy of individual component bodies of an isolated system may not only increase or remain constant, but also decrease, for instance, when heat is being transferred from a body.

Generalizing the results obtained for reversible and irreversible processes developing in an isolated system, Eqs. (8-15) and (8-16) can be presented in the following form

$$dS\geqslant 0. \tag{8-17}$$

The equality sign pertains to reversible, and the sign "more than"—to irreversible processes.

All real processes are irreversible, therefore the entropy of an isolated system always increases. The mere fact of the increase of entropy would seem to be of no great importance, however the increase of entropy in irreversible processes is associated with a decrease in the efficiency of an isolated system.

Let us consider an ideal machine operated on the Carnot cycle, in which heat Q_1 is added to the working medium at temperature T_1 and heat is rejected from it to a sink at temperature T_2. The positive work $L=Q_1-Q_2$.

The thermal efficiency of the cycle

$$\eta_t=(Q_1-Q_2)/Q_1=L/Q_1,$$

or

$$L=\eta_t Q_1=Q_1(1-T_2/T_1). \tag{8-18}$$

Let us introduce between the source at temperature T_1 and the working medium an intermediate heat source at temperature $T_2<T_1'<T_1$. First heat shall be transferred irreversibly (at a finite temperature difference) to the intermediate source, and from it, at temperature T_1'—to the working medium realizing a reversible Carnot cycle.

If heat Q_1 enters the machine at a lower temperature $T_1' < T_1$, it is clear that the positive work must diminish, since the temperature difference in which the Carnot cycle is realized decreases. Then

$$L' = Q_1 \eta_t' = Q_1(1 - T_2/T_1).$$

The decrease in efficiency of the working medium due to the introduction of an additional irreversible process of heat transfer from the high-temperature source to the intermediate heat source is determined from the equation

$$L_0 = L - L' = Q_1[(1 - T_2/T_1) - (1 - T_2/T_1')] = Q_1(T_2/T_1' - T_2/T_1),$$

or

$$L_0 = T_2(Q_1/T_1' - Q_1/T_1) = T_2 \Delta S_{sys}. \tag{8-19}$$

This equation is known as the *Gouy-Stodola equation.* The decrease in the availability of an isolated system in which irreversible processes take place is equal to the product of the increase of system entropy and the absolute temperature of the sink. This loss of efficiency represents the amount of heat uselessly transferred to the surrounding medium. All irreversible processes occurring in an isolated system are accompanied by a depreciation of energy which changes from a more useful into a less useful form. Scattering and degradation of energy takes place, accompanied by an increase in the entropy of the system.

All spontaneous, i.e. irreversible, processes always occur with an increase of entropy. Thus, the principle of increase of entropy of an isolated system is the general expression of the second law of thermodynamics.

8-11. Maximum Work. Exergy

Of great importance in thermodynamics is the concept of the work performed by an isolated, or closed, system upon a change in its state and in conditions in which maximum work is obtained.

Work can only be obtained from a system that is not in equilibrium with the surroundings, i.e. when in the general case pressure p_1 and temperature T_1 of the system are greater than the pressure p_0 and temperature T_0 of the interacting surrounding medium. As work is being produced the closed system shall approach a state of equilibrium with the surroundings.

If in an isolated system there are working media at different temperatures, then in such a system the working medium at a higher temperature can produce work (in an ideal case by realizing repeatedly the Carnot cycle). Such a process results in a decrease in the temperatures of the high-temperature sources and an increase in the temperatures of the low-temperature sources. When these temperatures become equal further production of work shall cease. Hence, the performance of work is associated with the passing of an isolated system from a state of non-equilibrium into an equilibrium state.

In the Carnot cycle maximum work can only be obtained when the temperature of the working medium is equal to the temperature of the source and when the minimum temperature of the working medium is equal to that of the sink, i.e. when reversible processes are realized. It follows from the foregoing that when a system passes from a non-equilibrium into an equilibrium state the maximum work can be obtained only upon the realization of reversible adiabatic and isothermal processes.

Let us consider what maximum work can be obtained from a working medium (gas) in given conditions. Let us assume the surroundings and the working medium to be isolated, adiabatic system to which heat is neither added nor rejected, i.e. $Q=0$. Let us denote the internal efficiency of the system in the initial and the final state by U' and U'', respectively. Then, based on the first law of thermodynamics, we have

$$U''-U'+L=Q=0,$$

whence the work produced is equal to

$$L=U'-U''. \tag{8-20}$$

The internal energy of the entire system is an additive quantity, equal to the sum of the energy of the surrounding medium and of the energy of the source of work.

Let us denote the initial and final values of the internal energy of the surrounding medium by U_{01} and U_{02}, of the source of work by U_1 and U_2, respectively, then

$$U'=U_1+U_{01} \quad \text{and} \quad U''=U_2+U_{02}$$

and

$$L=U_1+U_{01}-U_2-U_{02} \quad \text{or} \quad L=(U_1-U_2)+(U_{01}-U_{02}). \tag{8-21}$$

The working medium is capable of exchanging heat with the surrounding medium and performing work on it. Denoting by Q_0 the heat rejected from the working medium to the surroundings, and by L_0—the work performed by the working medium on the surroundings, we obtain

$$U_{02}-U_{01}=Q_0+L_0.$$

Since the pressure of the surrounding medium, p_0, is constant, then

$$L_0=p_0(V_2-V_1),$$

where V_1 and V_2 are the initial and final volumes of the working medium. Then

$$U_{01}-U_{02}=-Q_0-p_0(V_2-V_1). \tag{8-22}$$

Substituting the value of the change in internal energy of the surroundings from Eq. (8-22) into Eq. (8-21), we find that

$$L=(U_1-U_2)-Q_0-p_0(V_2-V_1). \tag{8-23}$$

The heat rejected to the surrounding medium, Q_0, is equal to the product of its constant temperature T_0 and the change of entropy of the surroundings

$$Q_0 = T_0(S_{02} - S_{01}). \tag{8-24}$$

Substituting Eq. (8-24) into Eq. (8-23), we obtain

$$L = (U_1 - U_2) - T_0(S_{02} - S_{01}) - p_0(V_2 - V_1). \tag{8-25}$$

Since a fraction of work $p_0 = (V_2 - V_1)$, expended to displace the surrounding medium (referred to as displacement work), is subtracted from the entire work, Eq. (8-25) determines the useful work performed by the system as it passes from the initial state into an equilibrium state.

From the well-known statement that, when reversible processes occur the entropy of an isolated adiabatic system does not change, it follows

$$S_{02} - S_{01} = S_1 - S_2,$$

where S_1 and S_2 are the entropies of the working medium in the initial and final states.

Replacing in Eq. (8-25) $(S_{02} - S_{01})$ with $(S_1 - S_2)$, we can write down the equation for the maximum work associated with reversible processes

$$L'_{max} = (U_1 - U_2) - T_0(S_1 - S_2) + p_0(V_1 - V_2). \tag{8-26}$$

Equation (8-26) shows that with given parameters p_0 and T_0 of the surrounding medium, the maximum useful work of a system is determined by the initial state of the working medium and is independent of the path along which the change of state occurs. It is impossible to obtain from a system an amount of work greater than the maximum.

For a maximum utilization of the efficiency of a source of work the following must be observed: $p_0 = p_2$ and $T_0 = T_2$. In these conditions all the other parameters of the working medium shall also be determined by the parameters of the surrounding medium, i.e.

$$U_2 = U_0 \quad \text{and} \quad V_2 = V_0.$$

Then, equation (8-26) reduces to

$$L'_{max} = (U_1 - U_0) - T_0(S_1 - S_0) + p_0(V_1 - V_0),$$

or

$$L'_{max} = (I_1 - I_0) - T_0(S_1 - S_0). \tag{8-27}$$

Here I_0 and S_0 are the enthalpy and entropy of the working medium in the state of equilibrium with the surrounding medium.

In Eq. (8-27) the quantity $(I_1 - I_2)$ represents the useful external work performed by the working medium in a reversible adiabatic process, and $T_0(S_1 - S_0)$—the useful external work of the working medium udergoing a reversible isothermal process. Consequently, as was stated above, the maximum useful work can be obtained from a working medium as it

changes its state from the initial to that of the surrounding medium when reversible adiabatic and isothermal processes are realized.

The maximum useful work calculated with the aid of Eq. (8-27) is called the *efficiency*, or full *exergy*, of a body. In the last few years the concept of exergy has been widely used in thermodynamic investigations of processes. The method of investigation involving exergy was given the name the *exergy method.*

In the general case, by specific exergy e is meant the specific efficiency of heat, or of the flow of a working medium in a system undergoing a reversible thermodynamic process of change in state from initial parameters to constant parameters of the surrounding medium. For the flow of a working medium such a reversible change can be realized by two reversible processes: adiabatic (with a change in temperature of the working medium from the initial T_1 to the surrounding temperature T_0), and isothermal (with a change in the pressure, corresponding to the end of the adiabatic process, to the pressure p_0 of the surrounding medium). The exergy of the flow of a working medium can, therefore, be determined by formula (8-27), written for 1 kg of the working medium

$$e=(i_1-i_0)-T(S_1-S_0).$$

If in any process involving a change in state the final properties differ from these of the surrounding medium, then the real work obtained in the process will be expressed as the difference between the exergies of the beginning and end of the process, i.e.

$$e_{real}=e_1-e_2.$$

The efficiency, or exergy, of heat is determined on the condition that maximum possible work can be obtained when a reversible Carnot cycle is realized between the initial temperature and the temperature of the surrounding medium. Then

$$de_q=dq\eta_t^{\text{Carnot}}=dq(1-T_0/T)$$

or for the entire process

$$e_q=\int_1^2(1-T_0/T)\,dq=(1-T_0/T_{av})q_{1\text{-}2},$$

where e_q = exergy efficiency of heat;
T_{av} = average temperature in the process.

If in any process the amount of exergy added into the system exceeds the amount of exergy transferred from it, the difference between the two quantities characterizes the loss of exergy due to the irreversibility of the process.

Hence, we can introduce the concept of the *exergy efficiency*, characterizing the degree of reversibility of a process.

The exergy efficiency is determined as

$$\eta_e = 1 - \Delta e / e_1,$$

where Δe = the difference between the added and rejected exergies;
e_1 = added exergy.

The new quantity proved to be rather convenient for determining the thermodynamic perfection of any heat apparatus or of its component parts and sections.

8-12. Entropy and the Statistical Nature of the Second Law of Thermodynamics

At the end of the 19th century a number of scientists (J. Maxwell, L. Boltzmann, J. Gibbs, R. Smoluchowski and others) proved in their studies that the second law of thermodynamics is not an absolute law of nature; it is of importance only for macroprocesses and cannot be applied to microsystems.

L. Boltzmann has suggested a statistical interpretation of the second law and pointed the limits of its applicability. Briefly, Boltzmann's theory can be set forth as follows.

Let us assume that a vessel, supposedly divided into two parts, accommodates one molecule. The probability* that this molecule is positioned at the given moment of time in the right-hand part of the vessel is equal to 50 per cent, or to 1/2, since it is equally probable that the molecule may be positioned in the left-hand part of the vessel.

If the vessel contains two molecules then, since the mathematical probability of two independent events is expressed by the product of two individual probabilities, the probability of the simultaneous detecting the two molecules in the right-hand part of the vessel is equal to $(1/2)\times(1/2)=1/4$. If n molecules are placed into the vessel then the probability of the simultaneous detecting all molecules in the right-hand part of the vessel will, clearly, be expressed by the fraction: $P=1/2^n$.

Taking into consideration the fact that even a small quantity of gas consists of an enormous number of molecules, it may be stated that the probability of detecting a great number of molecules in one part of the vessel is close to zero.

All spontaneous processes occurring from less probable states to more probable are irreversible and they are associated with an increase of entropy. There should, therefore, exist a link between the increase of system entropy and its change from a less probable state into a more probable one. Maximum entropy corresponds to a stable system equilibrium which is exactly the most probable state in the given conditions. It follows from

* Here by *probability* is meant the mathematical probability—the ratio of the number of favourable events to the number of equally like events.

this that the entropy S of an adiabatic system must be a function of the thermodynamic probability W* of its state

$$S=f(W).$$

Let us imagine a system separated into two parts. The entropies of the two parts are S_1 and S_2 and the probabilities of their states—W_1 and W_2; the entropy and the probability of the entire system are S and W. From the main Boltzmann's thesis it follows that

$$S_1=f(W_1); \quad S_2=f(W_2); \quad S=f(W).$$

The entropy of a system is an additive quantity, i.e. the entropy of a system is equal to the sum of entropies of its parts

$$S=S_1+S_2,$$

and the probability of the state of the system is equal to the product of the probabilities of individual component parts

$$W=W_1W_2,$$

or

$$S=f(W_1W_2)=f(W_1)+f(W_2).$$

Differentiating this equality with respect to W_1, denoting the obtained derivative of the function f by f', and taking into account that $f(W_2)$ is independent of (W_1), we obtain

$$f'(W_1W_2)W_2=f'(W_1).$$

Differentiating the same equality with respect to W_2, we obtain

$$f'=(W_1W_2)W_1=f'(W_2).$$

Let us multiply the first of the equations obtained by W_1, and the second—by W_2. The left-hand sides of the two equations become equal, hence, the right-hand sides must also be equal to each other

$$f'(W_1W_2)W_1W_2=f'(W_1)W_1;$$
$$f'(W_1W_2)W_1W_2=f'(W_2)W_2;$$
$$f'(W_1)W_1=f'(W_2)W_2.$$

Since the two parts of the system considered are absolutely arbitrary and consist of any kind of bodies, the last equality shows that for any arbitrary system

$$Wf'(W)=k,$$

*Here and below by *probability* is meant thermodynamic probability—the number of microstates comprising a given macrostate. The thermodynamic probability is expressed by a whole, usually very great number.

where k is Boltzmann's constant, i.e. the universal gas constant reduced to one molecule.

From the relationship $S=f(W)$ it follows that

$$f'W=\frac{dS}{dW}.$$

Comparing the last two equations, we find that

$$\frac{dS}{dW}=\frac{k}{W},$$

whence, upon integration we obtain

$$S=k \ln W+C.$$

The above equation is known as Boltzmann's equation relating the entropy of a system with the probability of its state. Entropy S of a closed system in an equilibrium and non-equilibrium states is proportional to the natural logarithm of the probability of a given state.

Whence, Boltzmann's statement of the second law of thermodynamics: "Any change in the state of a system proceed spontaneously only in the direction in which there may be a change from a less probable to a more probable distribution of the parts of the system."

Thus, L. Boltzmann has shown that the increase of entropy cannot be considered as something absolute.

L. Boltzmann was the first to indicate the statistical, relative nature of the second law of thermodynamics. He substantiated not only the possible increase of entropy in nature, but also its possible decrease (for instance, with fluctations)*.

However, notwithstanding the progressive nature of Boltzmann's ideas their weak point must be indicated. L. Boltzmann considered the universe as a system in absolute equilibrium, in which accidental deviations are encountered. This cannot be agreed to.

In "Dialectics of Nature", Engels indicated that from the point of view of dialectical materialism all the processes occurring in the universe are processes of endless and continuous self-development of matter. Continuous destruction and creation takes place in universe. Nature cannot be in a state of rest and immobility. Our knowledge of nature and of the processes developing in it is yet very restricted. There is no doubt that science shall discover processes that are accompanied by a decrease of entropy, i.e. science shall find out the way in which heat may convert into another form of motion in which it can again concentrate and begin to function actively.

* Accidental deviations of various physical quantities from their average or equilibrium values are called *fluctuations*.

8-13. On the Erroneous Generalizations of Clausius Concerning the Increase of Entropy in the Universe

An analysis of all natural spontaneous thermal processes shows that all of them are irreversible and are accompanied by an increase of entropy. In an adiabatic system these processes terminate as soon as thermal equilibrium sets in, with entropy reaching its maximum value.

This fact permitted Clausius to arrive at the non-substantiated and erroneous conclusion that "the entropy of the universe tends to some maximum". This conclusion of Clausius is equivalent to the assertion of the inevitable "death of universe through heat".

The ideas of Clausius were shared by other physicists of the last century. Thus, the English scientist G. Thomson wrote: "At the present time there is a general tendency in the material world toward the scattering of mechanical energy."

The physicist Th. Tate asserted that heat, distributed all around, and spilled uniformly everywhere is degenerated and it has no value whatsoever. And all energies of the universe shall have to adopt this degraded form.

Clausius' mistake consists in incompetence of the extension of the conclusions concerning the increase of entropy, true for finite adiabatic systems, to the infinite Universe. This idealistic conception, asserting essentially the finiteness of the Universe and its inevitable death, asserts at the same time the moment of its beginning, i.e. "creation". The point of view of the idealistic minded scientists on the second law of thermodynamics has contributed to the strengthening of position of religion, which got as a scientific substantiation of its teaching on the creation and end of the world.

In this connection the famous physicist Nernst wrote that the idea that all that takes place in the world has begun, so to say, on a one particular day and shall also end finally on a certain day is improbable to such an extent that any theory that indispensably leads to this conclusion should be considered highly improbable and therefore unsubstantiated.

That is why the second law of thermodynamics, yielding trustworthy results in terrestrial conditions for finite adiabatic systems, should not be extended to cover the entire Universe. Not only processes of irreversible scattering of energy take place in the world but also reverse processes resulting in a rebirth, regeneration, of energy and its concentration. New celestial worlds appear as is evidenced by recent studies.

Engels was the first to suggest that the matter radiated by the stars into outer, or cosmic, space must concentrate again and serve as the beginning for a new circulation of matter. The laws that govern the rebirth of energy are yet unknown, but problems concerning the appearance of worlds shall be solved by man, which is as true as the fact that no miracles take place in nature.

8-14. Absolute Thermodynamic Temperature

Temperature that characterizes the degree of hotness of bodies is one of the most important entities in modern science.

The measurement of the temperature of a body with the aid of gas- or liquid-filled thermometers is based on the individual properties of thermometric substances due to the unequal temperature-dependence of the coefficient of expansion of various fluids, liquids and gases. From this it follows that any measurement of the temperature of a body with the aid of thermometers does not make it possible to determine the temperature that does not depend on the individual properties of the substance (fluid) used.

Kelvin has suggested a method based on the second law of thermodynamics and independent of the properties of the substance used for a faultless determination of temperature.

If in a reversible Carnot cycle heat Q_1 at temperature T_1 is transferred to the working medium (irrespective of its nature) from a source and heat Q_2 is rejected from the working medium to a sink, at temperature T_2, the ratio of absolute temperatures T_1/T_2 is equal to the ratio of the amounts of heat added and rejected to Q_1/Q_2

$$\eta_t = 1 - Q_2/Q_1 = 1 - T_2/T_1 \quad \text{or} \quad Q_1/Q_2 = T_1/T_2 \tag{8-28}$$

Since the amounts of heat Q_1 and Q_2 can be measured preliminarily, then, selecting one fixed point at temperature T_2 and realizing a Carnot cycle in which the sink would be at temperature T_2, and the source—at temperature T_1, we can measure the temperature T_1 of a body on the basis of Eq. (2-28).

The temperature scale constructed in this way is known as the *thermodynamic temperature scale* or the *Kelvin scale* of temperature. As was already mentioned above, the Eleventh General Conference on Weights and Measures has adapted as the main temperature scale the thermodynamic scale on which temperature is measured in degrees K. This scale was constructed with the aid of one fixed point—the triple point of water at which the thermodynamic temperature was assigned the magnitude of 273.16 K (exact).

Thd lower limit of the Kelvin scale of temperature is absolute zero. Therefore, one degree K is equal to $\frac{1}{273.16}$ of the temperature interval between the triple point of water and absolute zero.

If a cycle is realized between a source at temperature T_1 and a sink into which an amount of heat equal to zero ($Q_2 = O$) is rejected, then the absolute temperature of the sink would have to be equal to zero. In these conditions the entire heat Q_1 would be converted into useful work $L = Q_1$, and the efficiency of the cycle would be equal to unity. Therefore, the zero on the absolute temperature scale is the lowest of all temperatures possible when the efficiency of a Carnot cycle is equal to unity. Such a temperature is

assumed to be the *initial point of the absolute thermodynamic temperature scale.*

Thus, the second law of thermodynamics makes it possible to determine temperature as a quantity that is independent of the nature of the working medium and it indicates the way to construct the absolute temperature scale.

8-15. Integral Mean Temperature

To simplify some thermodynamic investigations, the concept of integral mean temperature has been introduced.

On a *T-s* diagram the integral mean temperature is represented by the altitude of the rectangle the area of which is equal to the area under the curve of the process *1-2* (Fig. 8-9). Area *42134* represents on some scale the added heat q. It is clear that the integral mean temperature will be represented by the altitude of the rectangle *3465* equivalent to the area *42134*. It follows from this definition that

$$T_{in\,m}=\frac{\text{area } 42134}{3\text{-}4}=\frac{\text{area } 34653}{3\text{-}4},$$

but area $42134=\int_1^2 T\,ds=q$, and $3\text{-}4=s_2-s_1$,

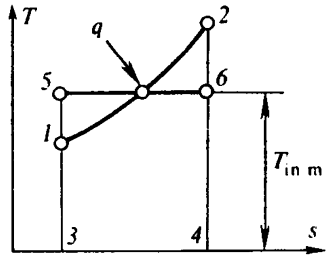


FIG. 8-9

therefore

$$T_{in\,m}=\frac{\int_1^2 T\,ds}{s_2-s_1}=\frac{q}{s_2-s_1} \qquad (8\text{-}29)$$

For any process the integral mean temperature is equal to the ratio of the amount of heat involved in the process to the change in the entropy of the working medium. Hence, the quantity of heat involved in the process is equal to the product of the integral mean temperature and the change of entropy in the given process. For instance, for any polytropic process

$$q=c_{pol}(T_2-T_1)=c_v\frac{n-k}{n-1}(T_2-T_1)$$

and

$$\Delta s=\int_{T_1}^{T_2} dq/T=\int_{T_1}^{T_2} c_{pol}(dT/T)=c_{pol}\ln T_2/T_1=c_v[(n-k)/(n-1)]\ln T_2/T_1.$$

Substituting the value of q and Δs into Eq. (8-29), we find

$$T_{in\,m}=\frac{c_v[(n-k)/(n-1)](T_2-T_1)}{c_v[(n-k)/(n-1)]\ln T_2/T_1}=\frac{T_2-T_1}{\ln T_2/T_1}. \qquad (8\text{-}30)$$

It follows from Eq. (8-30) that for any polytropic process the integral mean temperature only depends on the initial and final temperatures of the process.

Equation (8-29) can be used to determine the thermal efficiency of any arbitrary cycle in which the working medium undergoes adiabatic compression and expansion (Fig. 8-10). The amount of added heat $q_1=T_{1in\,m}(s_6-s_5)$, the amount of rejected heat $q_2=T_{2in\,m}(s_6-s_5)$. Then, the thermal efficiency of the arbitrary cycle is determined as

$$\eta_t=1-q_2/q_1=1-[T_{2in\,m}(s_6-s_5)/T_{1in\,m}(s_6-s_5)],$$

or

$$\eta_t=1-\frac{T_{2in\,m}}{T_{1in\,m}}. \qquad (8\text{-}31)$$

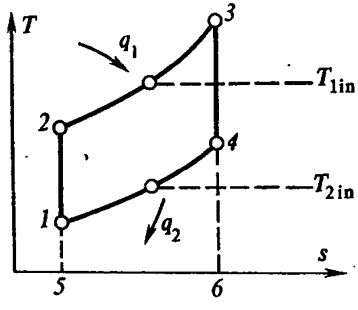


FIG. 8-10

The thermal efficiency of an arbitrary cycle is equal to the thermal efficiency of a Carnot cycle realized between the integral mean temperatures at which heat is added and rejected.

An analysis of Eq. (8-31) shows that the higher the integral mean temperature of heat addition and the lower the integral mean temperature of heat rejection, the higher the thermal efficiency of the cycle investigated. The limiting value for the thermal efficiency of an arbitrary cycle is the thermal efficiency of an ideal Carnot cycle, when the temperature $T_{2in\,m}$ turns into T_2, and $T_{1in\,m}$—into T_1. Consequently, a reversible Carnot cycle, realized in a certain temperature interval, possesses a higher thermal efficiency, compared with the thermal efficiency of any arbitrary cycle realized in the same temperature interval.

Typical Questions and Examples to Chapter Eight

1. Is it possible to utilize the internal energy of seas, oceans, or the surrounding air to continuously produce useful work?
2. Is it possible to convert into work all the heat added to the working medium in a cyclic process?
3. What are the main statements of the second law of thermodynamics?
4. What conditions must be ensured for continuous conversion of heat into work?
5. What is meant by a cyclic process or cycle?
6. Name the existing thermodynamic cycles.
7. What is meant by thermal efficiency?
8. In what conditons can the thermal efficiency of a thermodynamic cycle be equal to unity?
9. Describe the reversible Carnot cycle.

10. Derive the equation for the thermal efficiency of a reversible Carnot cycle.
11. What are the parameters on which the thermal efficiency of a reversible Carnot cycle depends?
12. Can the thermal efficiency of a reversible Carnot cycle be equal to unity?
13. Can a heat engine be operated with a thermal efficiency greater than that of the Carnot cycle?
14. Describe the reverse Carnot cycle.
15. What machines are operated on the reverse Carnot cycle?
16. What is meant by the refrigerating factor and how is it determined?
17. What is the essence of the Carnot theorem?
18. What are the properties of reversible Carnot cycles and what is meant by the first Clausius integral?
19. What are the properties of irreversible Carnot cycles and what is meant by the second Clausius integral?
20. Graphical representation of the generalized (regenerative) Carnot cycle on the *T-s* diagram and its efficiency.
21. How does the entropy change in a closed adiabatic system when reversible and irreversible processes develop in it?
22. Prove that in irreversible processes the efficiency of a body diminishes and entropy increases.
23. How is the maximum useful work, or efficiency, of a working medium determined?
24. What is meant by exergy?
25. Can exergy be considered a parameter of state?
26. The statistical nature of the second law of thermodynamics.
27. Boltzmann's theory.
28. Boltzmann's equation relating the entropy of a system to its probability.
29. The erroneous nature of Clausius' assumption concerning the heat death of the Universe.
30. How was Clausius assumption criticized in the works of Engels, Nernst and other scientists?
31. How is the integral mean temperature determined?
32. Express the thermal efficiency of an arbitrary cycle in terms of integral mean temperatures.

Example 8-1. In a counterflow heat exchanger air is heated from temperature $t_1=40$ °C and the gases are cooled from temperature $t_3=450$ °C to $t_4=200$ °C. The heat lost from the heat exchanger to the surroundings by radiation amounts to 20 per cent of the heat transferred from the gas. Determine the fall in efficiency per 1 kg of the gas flowing through the heat exchanger due to the irreversibility of the heat-transfer process. Assume the gas and air to be ideal gases possessing the properties of air. The heat capacities of the air and gas are assumed to be constant. Ambient temperature $t_0=25$ °C.

Determine the temperature t_2 to which the air is heated from the heat-balance equation:

$$0.8c_p(t_3-t_4)=c_p(t_2-t_1),$$

whence

$$t_2=0.8(t_3-t_4)+t_1=0.8(450-200)+40=240\ ^\circ\text{C}.$$

The heat lost per 1 kg of the flowing gas

$$q=0.2c_p(t_3-t_4)=0.2\times 1.0(450-200)=50.0\ \text{kJ/kg},$$

where

$$c_p=\frac{k}{k-1}R=1.0\ \text{kJ/kg K}.$$

The efficiency loss is determined from the equation

$$l_0=T_0\,\Delta s_{sys},$$

where T_0 = ambient air temperature;
Δs_{sys} = the sum of the changes of the entropy of gas Δs_1, of air Δs_2 and of the surrounding medium Δs_3, due to the transfer (loss) of heat to the surrounding medium by radiation.

The change of the entropy of the gas

$$\Delta s_1=c_p \ln T_4/T_3=1.0\times 2.3 \log 473/723=-0.425\ \text{kJ/kg K}.$$

The change of the entropy of the air

$$\Delta s_2=c_p \ln T_2/T_1=1.0\times 2.3 \log 513/313=+0.495\ \text{kJ/kg K}.$$

The change of the entropy of the surroundings

$$\Delta s_3=q/T_0=50/298=+0.168\ \text{kJ/kg K}.$$

The change of the entropy of the system

$$\Delta s_{sys}=\Delta s_1+\Delta s_2+\Delta s_3=-0.425+0.495+0.168=0.238\ \text{kJ/kg K}.$$

The efficiency loss per 1 kg of the flowing gas amounts to

$$l_0=T_0\,\Delta s_{sys}=298\times 0.238=71\ \text{kJ/kg}.$$

Example 8-2. Determine the efficiency (exergy) of 1 kg of air under a pressure $p_1=4.0$ MN/m^2 or $p_1=40$ bar at a temperature $t_1=500$ °C. The temperature and pressure of the surrounding medium are $t_0=27$ °C and $p_0=1$ bar. Solve the problem, assuming first a constant then a variable heat capacity.

The efficiency, or exergy, of air is determined from Eq. (8-27)

$$l_e=i_1-i_0-T_0(s_1-s_0),$$

$$l_e=c_p(t_1-t_0)-T_0(c_p \ln T_1/T_0-R \ln p_1/p_0)=1.0(500-27)-$$
$$-300(1.0\times 2.3 \log 773/300-0.287\times 2.3 \log 40/1)=310.0\ \text{kJ/kg},$$

where

$$c_p=\frac{k}{k-1}R=\frac{1.4}{0.4}0.287=1.0 \text{ kJ/kg K.}$$

The efficiency at a variable heat capacity

$$l_e=1.043[500-27-300(1.043\times 2.3 \log 773/300-0.287\times 2.3 \log 40)]=$$
$$=317.0 \text{ kJ/kg,}$$

where

$$c_p\Big|_{t_1}^{t_2}=\frac{c_{pm}\Big|_0^{t_2}t_2-c_{pm}\Big|_0^{t_1}t_1}{t_2-t_1}=\frac{1.0387\times 500-1.0043\times 27}{500-27}=1.043 \text{ kJ/kg K.}$$

Example 8-3. Determine the amount of heat that must be spent to heat polytropically 5 kg of air from $T_1=300$ K at a pressure $p_1=4$ bar to a temperature of 1000 K at a pressure of 10 bar. The heat capacity of air $c_p=1$ kJ/kg K.

Let us solve the problem, using Eq. (8-29)

$$Q=mT_{in\,m}(s_2-s_1).$$

In the given conditions the integral mean temperature

$$T_{in\,m}=\frac{T_2-T_1}{\ln T_2/T_1}=\frac{1000-300}{2.3 \log 1000/300}=582 \text{ K.}$$

The change of entropy per 1 kg of air amounts to

$$s_2-s_1=c_p \ln T_2/T_1-R \ln p_2/p_1=1.0\times 2.3\times 0.524-0.287\times 2.3\times 0.4=$$
$$=0.941 \text{ kJ/kg K.}$$

Then,

$$Q=mT_{in\,m}(s_2-s_1)=5\times 582\times 0.941=2738 \text{ kJ.}$$

Example 8-4. Determine the integral and arithmetic mean temperatures of a gas undergoing a polytropic process, assuming an initial gas temperature $T_1=800$ K and final $T_2=2000$ K.

The arithmetic mean temperature

$$T_{ar\,m}=\frac{800+2000}{2}=1400 \text{ K;}$$

the integral mean temperature

$$T_{in\,m}=\frac{T_2-T_1}{\ln T_2/T_1}=\frac{2000-800}{2.3 \log 2000/800}=1315 \text{ K.}$$

CHAPTER NINE

CHARACTERISTIC FUNCTIONS AND THERMODYNAMIC POTENTIALS. EQUILIBRIUM OF SYSTEMS

9-1. Properties of Characteristic Functions

As can be seen from the foregoing, the second law of thermodynamics can be used to solve the most diverse concrete practical problems. It proves, however, to be equally useful when applying the analytical method of analysis based on special functions of state, referred to as *characteristic functions.*

The name characteristic function of state is given to functions as well as their derivatives of various orders, that can be used to express explicitly all thermodynamic properties of a system, including the equations of state, calculation equations for the heat capacities C_p and C_v, and also the thermodynamic potentials (see below). The characteristic functions include internal energy $U(V, S)$, enthalpy $I(p, S)$, the isochoric-isothermal potential $F(T, V)$, the isobaric potential $Z(p, T)$, entropy $S(V, U)$ and volume $V(S, U)$.

Hence, if the analytical description of these functions is known in the independent parameters of the system, it is possible to obtain in an explicit form all basic thermodynamic quantities, characterizing the given system. The characteristic functions are additive: for a complex system they are equal to the sum of the values of these functions for individual components of the system. The differentials of characteristic functions are total differentials.

Starting from the mathematical expressions, or equations, of the first and second laws of thermodynamics, we obtain an expression that relates the two laws

$$T\,ds = dU + p\,dV. \tag{9-1}$$

As is known from the foregoing, this expression is called the *thermodynamic identity.* It only contains parameters, functions of state of the system, their differentials and pertains to reversible processes. When expressed in terms of the variables p and T the thermodynamic identity (9-1) takes the form

$$T\,ds = dI - V\,dp. \tag{9-2}$$

Equations (9-1) and (9-2) are the most general equations of thermodynamics. They interrelate five variable quantities T, S, U, p, V determining the state of the system. These five parameters can be used to compose ten different pairs of parameters: U, T; U, S; U, p; U, V; T, S; T, V; T, p;

S, p; S, V; p, V. Only four of them are of paramount importance for thermodynamic investigations, namely:

$U=U(S, V)$—internal energy;

$I=I(S, p)$—enthalpy;

$F=F(T, V)$—isochoric-isothermal potential;

$Z=Z(T, p)$—isobaric-isothermal or isobaric potential.

Internal energy U is a characteristic function when S and V are independent variables. If a system performs work, the equation expressing the change of internal energy takes the form

$$dU=T\,dS-p\,dV \tag{9-3}$$

With $V=\text{const}$ and $S=\text{const}$ Eq. (9-3) can be used to obtain by simple differentiation

$$T=(\partial U/\partial S)_V; \quad p=-(\partial U/\partial V)_S \tag{9-4}$$

Then

$$I=U+pV=U-V(\partial U/\partial V)_S. \tag{9-5}$$

Taking the second derivatives of $U(S, V)$, we can determine the caloric coefficients

$$(\partial^2 U/\partial S^2)_V=(\partial T/\partial S)_V=T(\partial T/T\partial S)_V=T(\partial T/\partial q)_V=T/C_V,$$

whence

$$C_v=\frac{T}{(\partial^2 U/\partial S^2)_V} \tag{9-6}$$

From Eq. (9-4) we find

$$(\partial^2 U/\partial V^2)_S=(dp/dV)_S.$$

Starting from Eq. (9-4), and by cross differentiation of the parameters we obtain

$$\frac{\partial^2 U}{\partial S\,\partial V}=\left(\frac{\partial T}{\partial V}\right)_S \quad \text{and} \quad \frac{\partial^2 U}{\partial V\,\partial S}=-\left(\frac{\partial p}{\partial S}\right)_V. \tag{9-7}$$

Equating the second derivatives, we find the so-called Maxwell relation

$$-(\partial p/\partial S)_V=(\partial T/\partial V)_S \quad \text{or} \quad (dS/dp)_V=-(\partial V/\partial T)_S. \tag{9-8}$$

Thus, expressed in terms of variables S and V, the internal energy U is a characteristic function that can be used to determine all the thermodynamic properties of the system: the first derivatives determine the thermal properties, and the second derivatives—the caloric properties.

The enthalpy I is a characteristic function when S and P are independent variables. Considering Eq. (9-2), we obtain

$$dI=T\,dS+V\,dp. \tag{9-9}$$

At $p=\text{const}$ and $S=\text{const}$, making use of Eq. (9-9), we can obtain by simple differentiation the values of the partial derivatives

$$T=(\partial I/\partial S)_p, \quad V=(\partial I/\partial p)_S \tag{9-10}$$

and

$$U=I-pV=I-p(\partial I/\partial p)_S. \tag{9-11}$$

Departing from Eq. (9-10), by means of cross differentiation of parameters, let us compose the combined second derivatives of the function I and, equating them by analogy with Eq. (9-8), we obtain the second Maxwell relation

$$(\partial T/\partial p)_S=(\partial V/\partial S)_p \quad \text{or} \quad (\partial p/\partial T)_S=(dS/dV)_p \tag{9-12}$$

In addition, at $p=\text{const}$, the second derivatives of I with respect to S permit the heat capacity C_p to be determined from Eq. (9-6):

$$(\partial T/\partial S)_p=(\partial^2 I/\partial S^2)_p, \quad \text{but } dq_p=c_p\,dT_p=T\,dS_p,$$

or

$$(\partial T/\partial S)_p=T/C_p.$$

Whence

$$C_p=\frac{T}{(\partial^2 I/\partial S^2)_p}. \tag{9-13}$$

If temperature and volume are independent variables, then the characteristic function shall be the isochoric-isothermal potential F. The meaning of this name shall be clear from the following treatment. Subtracting $d(TS)$ from the left- and right-hand sides of Eq. (9-1), we obtain

$$dU-d(TS)=T\,dS-p\,dV-d(TS);$$

$$d(U-TS)=T\,dS-p\,dV-T\,dS-S\,dT, \tag{9-14}$$

and

$$dF=d(U-TS)=-S\,dT-p\,dV, \tag{9-15}$$

whence

$$dF=d(U-TS) \quad \text{or} \quad F=U-TS. \tag{9-16}$$

The quantity TS, which is also a function of state, is sometimes referred to as the *bound energy* (see Sec. 9-2).

Simple differentiation at $T=\text{const}$ and $V=\text{const}$ makes it possible to get from Eq. (9-15) the values of other parameters

$$S=-(\partial F/\partial T)_V; \quad p=-(\partial F/\partial V)_T; \tag{9-17}$$

$$U=F+TS=F-T(\partial F/T)_V, \tag{9-18}$$

$$I=U+pV=F+Ts+pV=F-T(\partial F/\partial T)_V-V(\partial F/\partial V)_T. \tag{9-19}$$

From the second equation (9-17) we can derive the thermal equation of state. In fact, expressing F in terms of V and T, i.e. $F=F(V, T)$, we obtain $p=p(V, T)$.

From Eqs. (9-17), let us compose the combined second derivatives of the function F, and equating the derivatives, we obtain the third Maxwell relation

$$(\partial p/\partial T)_V=(\partial S/\partial V)_T. \tag{9-20}$$

The isochoric-isothermal potential F is convenient for experimental investigations in that the independent variables V and T can be easily measured.

The second derivatives of the function $F(V, T)$ in respect to T and V permit determination of the heat capacity C_V. Let us make use of Eq. (9-17) from which it follows that

$$-(\partial S/\partial T)_V=(\partial^2 F/\partial T^2)_V,$$

but $dQ_V=C_V\,dT_V=T\,dS_V$, whence $(\partial S/\partial T)_V=C_V/T$, or

$$C_V=-T(\partial^2 F/\partial T^2)_V. \tag{9-21}$$

If the system temperature and pressure are independent parameters of state, the characteristic function shall be the isobaric potential $Z(T, p)$.

Adding the quantity $d(p, V)$ to the right- and left-hand sides of Eq. (9-11), we obtain

$$dF+d(pV)=-S\,dT-p\,dV+d(pV); \tag{9-22}$$

$$dZ=d(F+pV)=d(U-TS+pV)=-S\,dT+V\,dp; \tag{9-23}$$

$$dZ=d(U-TS+pV) \text{ or} \tag{9-24}$$

$$Z=U-TS+pV=1-TS.$$

The left-hand side of Eq. (9-23) is the total differential of the function when T and p are independent variables.

Differentiating Eq. (9-23) at $T=$const and $p=$const, we obtain the values of the other parameters

$$V=(\partial Z/\partial p)_T; \quad S=-(\partial Z/\partial T)_p; \tag{9-25}$$

$$U=Z+TS-pV=Z-T(\partial Z/\partial T)_p-p(\partial Z/\partial p)_p; \tag{9-26}$$

$$I=Z+TS=Z-T(\partial Z/\partial T)_p; \tag{9-27}$$

$$F=Z-pV=Z-p(\partial Z/\partial p)_T. \tag{9-28}$$

Equating the second derivatives of Eq. (9-25), we find the fourth Maxwell relation

$$(\partial V/\partial T)_p=-(\partial S/\partial p)_T. \tag{9-29}$$

The second derivatives of $Z(T, p)$ in respect to S and p permit determination of the heat capacity C_p

$$S=-(\partial Z/\partial T)_p; \quad (\partial S/\partial T)_p=-(\partial^2 Z/\partial T^2)_p=\frac{C_p}{T}; \tag{9-30}$$

$$C_p=-T(\partial^2 Z/\partial T^2)_p.$$

The thermodynamic functions are interrelated so that when some of them are known, the others can be determined.

Knowing the isochoric-isothermal potential F or the isobaric potential Z, it is easy to find the internal energy

$$U=F-TS=F-T(\partial F/\partial T)_V; \tag{9-31}$$

$$U=Z+TS-pV=Z-T(\partial Z/\partial T)_p-p(dZ/\partial p)_T. \tag{9-32}$$

Knowing Z, we can find enthalpy I

$$I=U+pV=Z+TS=Z-T(\partial Z/\partial T)_p. \tag{9-33}$$

It is possible to represent graphically the relationships between characteristic functions: the internal energy U, the enthalpy I, the isochoric-isothermal potential F and the isobaric potential Z, and also the bound energy TS (Fig. 9-1). In addition to the main four characteristic functions

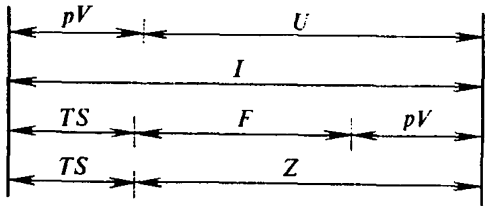


FIG. 9-1

U, F, I, Z, the entropy S is also used. If U and V are independent parameters of a system, then entropy S shall be the characteristic function.

In fact,

$$T\,dS=du+p\,dV; \quad dS=\frac{dU}{T}+p\frac{dV}{V};$$

$$T=\left(\frac{\partial U}{\partial S}\right)_V=\frac{1}{\left(\frac{\partial S}{\partial U}\right)_V}; \tag{9-34}$$

$$p=(\partial S/\partial V)_U(\partial U/\partial S)_V=\frac{(\partial S/\partial V)_U}{(\partial S/\partial U)_V}. \tag{9-35}$$

9-2. Physical Meaning of the Isochoric-Isothermal and Isobaric-Isothermal Potentials

Each characteristic function has its proper field of application: the isochoric-isothermal potential is used to analyze isochoric-isothermal processes, and the isobaric-isothermal potential is used in investigating isobaric-isothermal processes.

Let us consider the physical meaning of the isochoric-isothermal potential in Eqs. (9-15) and (9-16)

$$F=U-TS \quad \text{and} \quad dF=-S\,dT-p\,dV.$$

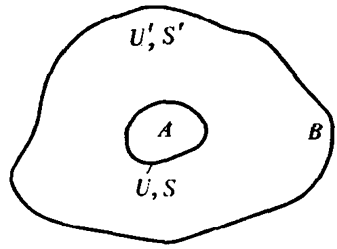


FIG. 9-2

Let us imagine the adiabatic system A considered as a part of another adiabatic system B (surrounding medium), shown in Fig. 9-2. The temperature of the two systems is T. Different constant-temperature processes take place inside the two systems. Let us denote the change of the internal energy and entropy of system A by dU and dS, and the change of the internal energy and entropy of system B—by dU' and dS'. In accordance with the law of conservation of energy, the internal energy of the entire closed complex system is constant

$$dU+dU'=0. \tag{9-36}$$

On the basis of the second law of thermodynamics the entropy of the complex system must either remain constant or, in the event of irreversible processes, increase:

$$dS+dS'\geqslant 0. \tag{9-37}$$

Let us assume that system A performs work dL on the component bodies of the surrounding medium B, transferring at the same time a certain quantity of heat to the surrounding medium B, resulting in an increase dS' in the entropy of the surrounding medium. Then, based on the thermodynamic identity (9-1), the change in the internal energy of the surrounding medium B shall be

$$dU'=T\,dS'+dL. \tag{9-38}$$

Work is positive if it is done on the component bodies of the surrounding medium and increases the energy of the bodies. From the above three equations we find that

$$dU-T\,dS\leqslant -dL. \tag{9-39}$$

In Eq. (9-39) all the quantities pertain to the system and not to the surrounding medium. Since the temperature of the complex system is constant, equation (9-39) can be reduced into

$$d(U+TS)\leqslant -dL.$$

But the bracketed expression is nothing but the isochoric-isothermal potential F, therefore for any isothermal processes

$$dF \leqslant -dL. \tag{9-40}$$

For reversible isothermal processes

$$dF = -dL, \quad \text{or} \quad -dF = dL.$$

The work done by a system undergoing reversible isothermal processes is equal to the decrease of its isochoric-isothermal potential.

It follows from Eqs. (9-16) and (9-40) that

$$-d(U-TS) = dL,$$

or at a constant temperature

$$-dU + T\,dS = dL. \tag{9-40a}$$

The quantity $T\,dS$ is the heat added to the system, therefore Eq. (9-40a) shows that in an isothermal process work is done not only at the expense of the internal energy of the system, but also at the cost of heat of the surroundings. The work is equal to the difference between dU and the added heat $T\,dS$

$$dL = -(dU - T\,dS),$$

or

$$dL = -d(U-TS) = -dF. \tag{9-40b}$$

The work is equal to the decrease in the isochoric-isothermal potential F. The isochoric-isothermal potential of the system, F, is a fraction of the energy that converts into external work in an isothermal process.

Thus, the total energy U of the system can be represented as the sum of two fractions [Eqs. (9-40) and (9-40b)]

$$U = F + TS.$$

The external isothermal work is done only at the expense of the isochoric-isothermal potential, while the fraction TS is liberated in the form of heat and performs no work. Helmholtz named this fraction as the bound energy.

In a reversible process the work performed by a body as it passes from one state into another is the maximum work. Then, integrating Eq. (9-40) between the initial and final states, we obtain

$$L_{max} = F_1 - F_2'. \tag{9-40c}$$

The maximum work done by a system undergoing an isothermal process is equal to the difference between the isochoric-isothermal potentials in its two states.

In an irreversible isothermal process the work dL done by the system shall be less than dL_{max}.

It follows from Eq. (9-40c) that

$$dL < -dF,$$

or upon integration we obtain

$$F_2 - F_1 < -L. \tag{9-40d}$$

It can be seen from the above inequality that the isochoric-isothermal potential of a system undergoing an irreversible isothermal process increases by a quantity less than the external work.

Equations (9-40c) and (9-40d) can be united

$$F_2 - F_1 \leqslant -L. \tag{9-41}$$

The equality sign pertains to reversible, the "less than" sign—to irreversible processes. In this way the isochoric-isothermal potential is the measure of the availability of the system at $T = \text{const}$.

If an irreversible process occurs at a constant volume and constant temperature and no external work is performed, the total work output of the system dL shall be equal to zero and Eq. (9-41) reduces into

$$F_2 - F_1 \leqslant 0 \tag{9-42}$$

The isochoric-isothermal potential of a system undergoing an irreversible process at a constant volume and temperature always diminishes, and it remains constant in a reversible process.

It should be noted that in a homogeneous system a process developing at constant temperature and volume can only be irreversible, otherwise the state of the system would be fully determined by giving the specific volume and temperature and no processes could occur in these conditions (the system would be in a state of equilibrium). In reality, processes can be realized at constant V and T when a chemical reaction proceeds in a mixture of reacting substances, when substances are being dissolved, etc.

Another equation for maximum work can be obtained, making use of Eq. (9-18)

$$F = U + T(\partial F/\partial T)_V.$$

Let a system pass from a first into a second state, then

$$F_1 = U_1 + T(\partial F_1/\partial T)_V; \quad F_2 = U_2 + T(\partial F_2/\partial T)_V.$$

The difference between the isochoric-isothermal potentials of the two states

$$L_{max} = F_1 - F_2 = U_1 - U_2 - T\frac{\partial}{\partial T}(F_1 - F_2)_V,$$

$$L_{max} = -\Delta U + T(\partial L_{max}/\partial T)_V.$$

In an isochoric process $U_1 - U_2 = -Q_V$, therefore

$$L_{max} = -Q_V + T(\partial L_{max}/\partial T)_V. \tag{9-43}$$

Equation (9-43) is known as the *Gibbs-Helmholtz equation for maximum work* at constant T and V.

Of great importance is the study of equilibrium in isobaric-isothermal processes.

The work of expansion done by a system overcoming the external pressure p is equal to

$$dL=p\,dV.$$

Substituting this expression into Eq. (9-40), we obtain

$$dF+p\,dV\leqslant 0,$$

or, applying Eq. (9-16), we find that

$$d(U-TS)+p\,dV\leqslant 0.$$

In the system under consideration, the pressure is constant, therefore the last equation can be presented in the following form

$$d(U-TS+pV)\leqslant 0.$$

But the expression in the brackets is the isobaric-isothermal potential [see Eq. (9-24)], therefore

$$dZ\leqslant 0 \quad \text{or} \quad Z_2-Z_1\leqslant 0. \tag{9-44}$$

It follows that in systems at a constant temperature and pressure reversible processes occur at a constant value of the isobaric potential. When irreversible processes develop in a system the isobaric-isothermal potential always diminishes.

It should be noted that in a homogeneous system at a constant temperature and pressure, placed in a surrounding medium at a constant pressure and temperature, a process can occur only if the parameters of the system differ from those of the surrounding medium. In a non-homogeneous two-phase system for which pressure and temperature are not independent variables reversible processes can occur when system pressure and temperature are equal to the pressure and temperature of the surrounding medium.

The equation of maximum work for an isobaric-isothermal process can be presented in the detailed form

$$L_{max}=Z_1-Z_2=(U_1+p_1V_1-TS_1)-(U_2+p_2V_2-TS_2), \tag{9-45}$$

or

$$L_{max}=(I_1-TS_1)-(I_2-TS_2). \tag{9-46}$$

It follows from Eq. (9.25) that

$$S_1=-\left(\frac{\partial Z_1}{\partial T}\right)_p \quad \text{and} \quad S_2=-\left(\frac{\partial Z_2}{\partial T}\right)_p. \tag{9-47}$$

Substituting the values of entropy into the equation of maximum work, we obtain

$$L_{max}=\left[I_1+T\left(\frac{\partial Z_1}{\partial T}\right)_p\right]-\left[I_2+T\left(\frac{\partial Z_2}{\partial T}\right)_p\right],$$

or

$$L_{max}=I_1-I_2+T\left[\frac{\partial(Z_1-Z_2)}{\partial T}\right]_p$$

but in an isobaric process

$$I_1-I_2=-Q_p, \quad \text{and} \quad Z_1-Z_2=L_{max},$$

therefore

$$L_{max}=-Q_p+T\left(\frac{dL_{max}}{\partial T}\right)_p. \tag{9-48}$$

Equation (9-48) is known as the *Gibbs-Helmholtz equation for maximum work* at constant T and p.

In a system in which an irreversible process develops at constant pressure and temperature the useful work is equal to

$$L_{use}=L_{max}-T_0\,\Delta S. \tag{9-49}$$

i.e. the useful work is smaller than the maximum work by the product of absolute temperature of the surrounding medium and the increase in system entropy. The quantity $T_0\Delta S$ is called the *loss of useful work due to process irreversibility.*

The characteristic functions $U(V, S)$, $I(p, S)$, $F(T, V)$ and $Z(p, T)$, full determining the thermodynamic properties of a system, are also referred to as thermodynamic potentials.

Thermodynamic potential is the name given to a characteristic function, the decrease of which in the equilibrium process, occurring at a constant pair of definite thermodynamic parameters (T and V; T and p; S and p; S and V), is equal to the entire work performed by the system less the work done against external pressure (work on the surrounding medium).

Each of the thermodynamic potentials is a function of the state of the system.

We know from the foregoing that in a reversible process for a body to be transferred from one state into another a minimum amount of work must be spent, and the work performed by the body itself as it passes from one state into another will be maximum. That is why the thermodynamic potentials permit determination of the maximum work done with different independent variables. In fact, with constant independent variables S and V the characteristic function and the thermodynamic potential is the internal energy U (the isochoric-isentropic potential), and

$$-dL_{max}=dU \quad \text{or} \quad L_{max}=(U_1-U_2)_{S,V}. \tag{9-50}$$

In an isochoric-isentropic process the maximum work of change in volume is equal to the decrease of the internal energy of the body involved.

With constant independent variables S and p the characteristic function and the thermodynamic potential is enthalpy I (isobaric-isentropic potential), and

$$-dL'_{max}=dI \quad \text{or} \quad L'_{max}=(I_1-I_2)_{p,S}. \tag{9-51}$$

In an isobaric-isentropic process the maximum useful external work is equal to the decrease of the enthalpy of the body.

With constant independent variables T and V the characteristic function and the thermodynamic potential is the isochoric-isothermal potential $F=U-TS$:

$$-dL_{max}=dF \quad \text{or} \quad L_{max}=(F_1-F_2)_{T,V} \tag{9-52}$$

In an isochoric-isothermal process the maximum work of change in volume is equal to the decrease of the isochoric-isothermal potential.

With constant independent variables p and T the characteristic function and the thermodynamic potential is the isobaric-isothermal potential, and

$$-dL'_{max}=dZ \quad \text{or} \quad L'_{max}=(Z_1-Z_2)_{p,T}. \tag{9-53}$$

In an isobaric-isothermal process the maximum useful external work is equal to the decrease of the isobaric-isothermal potential.

Thus, the knowledge of even one thermodynamic potential permits determination of the thermal and caloric properties of a thermodynamic system.

In practical investigations only two potentials are generally employed: the isochoric-isothermal potential and the isobaric potential, inasmuch as the independent variables T, V and T, p respectively associated with these potentials can easily be determined experimentally. All thermodynamic potentials are additive quantities and unambiguous, or single-valued, functions of state and their decrease in appropriate conditions determines the work done by the bodies acting upon a thermodynamic system.

Characteristic functions permit thermodynamic investigations of any both reversible and irreversible processes, and the use of partial differential equations simplifies to a great extent these investigations.

9-3. Chemical Potential

In considering the characteristic functions $U(V, S)$, $I(p, S)$, $F(T, V)$ and $Z(T, p)$ it was pointed out that they are additive or extensive quantities. But for a homogeneous system consisting of several components, any extensive quantity depends essentially on the composition of the system. If the mass m of any body increases several times, the magnitude of the characteristic functions U, I, F, Z of the given body must increase the same number of times.

The isobaric potential of a homogeneous system is a function of temperature, pressure, and also of the composition of the system, i.e. a function of the mass of all component substances of the system

$$Z=mz(p, T).$$

It is clear that other characteristic functions are equal to

$$U=mu(v, s); \quad I=mi(p, s); \quad F=mf(T, u).$$

The isobaric potential reduced to unit mass of a homogeneous system is called the *chemical potential;* it is equal to

$$z=i-sT=u+pv-sT. \tag{a}$$

With account taken of the thermodynamic identity $T\,ds=di-v\,dp$, the differential of the chemical potential dz is equal to

$$dz=-s\,dT+v\,dp.$$

If the quantity of a substance or its mass is considered to be a variable parameter that can acquire different values, just as other parameters that characterize the system, then the expression for the differentials of all thermodynamic potentials shall contain a supplementary term, containing the differential of the mass of the body, dm. In fact, differentiating the equation $U=mu$, we get

$$dU=m\,du+u\,dm=m(T\,ds-p\,dv)+u\,dm.$$

Since

$$m\,ds=d(ms)-s\,dm=dS-s\,dm,$$

$$m\,dv=d(mv)-v\,dm=dV-v\,dm,$$

then

$$dU=T\,dS-p\,dV+dm(u-Ts+pv);$$

or in accordance with Eq. (a)

$$dU=T\,dS-p\,dV+z\,dm.$$

By analogy, with the aid of Eq. (a), we obtain for dI, dF and dZ

$$\left.\begin{aligned} dI&=T\,ds+V\,dp+z\,dm,\\ dF&=-S\,dT-p\,dV+z\,dm,\\ dZ&=-S\,dT+V\,dp+z\,dm. \end{aligned}\right\} \tag{b}$$

It follows from Eq. (b) that

$$z=(\partial U/\partial m)_{v,s}=(\partial I/\partial m)_{p,s}=(\partial F/\partial m)_{T,v}=(\partial Z/\partial m)_{p,T}, \tag{9-54}$$

all these partial derivatives are equal to one another.

The chemical potential z is the partial derivative of any thermodynamic potential of the system with respect to the mass m of the body at constant values of corresponding independent variables.

It was indicated above that, taken with an opposite sign, the differentials dU, dI, dF and dZ represent the maximum useful external work that can be performed by a system placed in a surrounding medium at constant pressure and temperature and undergoing an infinitely small process. Then, it follows from Eq. (9-54) that the chemical potential is equal numerically to the maximum useful work transferred under these conditions from the system to the surroundings upon a reversible decrease of the mass of the system by unit mass. As applied to chemical reactions the chemical potential represents the maximum useful work that can be done by a reacting body on an external object as the mass of the body decreases by unit mass.

9-4. Thermodynamic Theory of Equilibrium

The thermodynamic theory of equilibrium which is a corrollary of the second law of thermodynamics finds a very extensive field of application in studying and investigating many physical and chemical processes.

All thermodynamic systems are subdivided into two main classes: homogeneous and heterogeneous, and each system may be in a state of stable or unstable equilibrium.

By *homogeneous* are meant systems inside which there are no interfaces separating their macroscopic parts from each other. Examples of homogeneous systems are mixtures of gases, liquid and solid solutions and also any chemically homogeneous body in any one of the various states of aggregation (solid, liquid or gaseous).

By *heterogeneous* are meant systems composed of several physically homogeneous bodies differing from each other and referred to as phases. Such systems may represent different states of aggregation of one and the same substance, or these bodies are products of mutual dissolution or products of chemical interaction of various substances. Examples of heterogeneous systems are ice—water, water—steam, grey and white tin, aqueous solution of salt—solid salt—water vapour, liquid metal alloy—solid solution of one metal in another, etc.

Each component phase of a heterogeneous system is a physically homogeneous body, capable upon a disturbance of equilibrium of exchanging its substance with other bodies, which is isolated from other bodies by an interface, and can be separated from other phases by mechanical means. If a heterogeneous system is not in equilibrium, its component substances may undergo a change of phase, for instance, the substance may turn from liquid into solid or vapour (gaseous) state, turn from one crystalline form into another. States of aggregation should not be confused with phases. There may be only three states of aggregation: solid, liquid and gaseous, and there may exist a greater number of phases. Experimental studies point towards the existence of two kinds of phase changes. Phase changes of the

first kind are accompanied by the absorption or evolution of latent heat of phase conversion and an abrupt change of the specific volume and entropy on the change-of-phase line; phase changes of the first kind include fusion, evaporation, sublimation, etc. Phase changes of the second kind are not accompanied by the absorption or evolution of heat and an abrupt change of specific volume and entropy. An example of a change of phase of the second kind is the transformation of ferromagnetic bodies at a temperature, called the *Curie point* or temperature, above which bodies lose their ferromagnetic properties; the transformation of ordinary metals into superconductors at low temperatures, etc.

A thermodynamic system may be in a state of *stable* or *unstable* (labile) equilibrium. When the system in stable equilibrium is brought out of the state of equilibrium by some external disturbance, it returns spontaneously to the initial state of stable equilibrium after the disturbance is removed. Consequently, to bring the system out of the state of stable equilibrium some work must be done on the system.

Unstable equilibrium differs from stable equilibrium in that the system brought out of the state of labile equilibrium, does not return into the initial state, but passes into a *new* state of stable equilibrium.

Due to the action of various disturbing factors, a system may be in a state of unstable equilibrium only for a short time. It then passes into a state of stable equilibrium.

States of equilibrium that are not influenced by some slight external disturbances and are unstable in respect to other disturbances are called the *states of relatively stable equilibrium* (the metastable states). Systems that are in a metastable state of equilibrium pass into a stable state after a certain period of time given the necessary conditions. An example of such a state is the state of supercooled water or the state of supersaturated vapour.

9-5. General Conditions for Equilibrium of a Thermodynamic System

In any simple or complex thermodynamic system that is not in equilibrium (e.g. if there is a pressure or temperature difference in the system) spontaneous processes originate without fail that sooner or later must bring the system into a state of stable equilibrium. Stable equilibrium is characterized by that the reasons causing the non-equilibrium processes are removed and the system returns spontaneously into the initial state. Any thermodynamic system that interacts with the surroundings having constant parameters acquires with time stable equilibrium, irrespective of the initial conditions.

The above derived thermodynamic potentials, and also entropy can serve as quantities indicating the direction of a process and characterize the conditions for stable equilibrium in any thermodynamic systems.

Let us consider an isolated (from external influences) thermodynamic system in which the internal energy U and the total volume V are constant

and in which any non-equilibrium processes take place. Since, being irreversible, all these processes proceed in one and the same direction, the entropy of the system increases continuously: $dS>0$. When stable equilibrium sets in in the system at constant internal energy and volume and all processes occurring in it terminate, entropy shall cease to increase, i.e. in the state of stable equilibrium system entropy shall be maximum

$$(\partial S)_{U,V}=0; \quad (\partial^2 S)_{U,V}<0. \tag{9-55}$$

As is known from mathematics, Eq. (9-55) characterizes the conditions for maximum entropy S. In an irreversible adiabatic process entropy can only increase and, consequently, stable equilibrium shall set in when entropy reaches its maximum value, $S=S_{max}$.

From the identity equation

$$dU=T\,dS-p\,dV,$$

it follows that at $S=\text{const}$ and $V=\text{const}$ the internal energy of a system becomes maximum, i.e.

$$(\partial U)_{S,V}=0; \quad (\partial^2 U)_{S,V}>0. \tag{9-56}$$

Consequently, in all non-equilibrium isochoric-isentropic processes internal energy U can only decrease and in the state of equilibrium $U=U_{\min}$.

Let us prove that in equilibrium conditions enthalpy also acquires its minimum value. The change of enthalpy in an irreversible process can be obtained from the identity equation (9-2)

$$dI=T\,dS+V\,dp.$$

With p and S constant the enthalpy I (isobaric-isentropic process) reaches a minimum

$$(\partial I)_{S,p}=0; \quad (\partial^2 I)_{S,p}>0. \tag{9-57}$$

Due to the fact that in an irreversible process occurring at constant S and p the enthalpy I decreases as the system approaches a state of equilibrium, in conditions of stable equilibrium it acquires a minimum value: $I=I_{\min}$.

For the system at constant temperature T and volume V the conditions of stable equilibrium can be obtained analyzing Eq. (9-42). The analysis shows that in reversible processes the isochoric-isothermal potential F remains constant, and in irreversible processes this potential always decreases

$$(F_2-F_1)_{V,T}\leqslant 0.$$

Therefore, in the conditions for system equilibrium the change of the isochoric-isothermal potential becomes equal to zero

$$(\partial F)_{V,T}=0; \quad (\partial^2 F)_{V,T}>0, \tag{9-58}$$

and the isochoric-isothermal potential itself acquires a minimum value: $F=F_{min}$.

Special attention should be paid to the condition of equilibrium in isothermal systems at a constant pressure. The characteristic function then will be the isobaric-isothermal potential, as it was shown above.

It follows from Eq. (9-54) that in systems at constant temperature T and pressure p reversible processes occur at a constant isobaric potential; but if irreversible processes occur in the system, the isobaric potential can only diminish

$$(Z_2-Z_1)_{p,T}\leqslant 0.$$

Therefore, in the conditions for system equilibrium the changes of the isobaric potential amount to

$$(\partial Z)_{p,T}=0, \quad (\partial^2 Z)_{p,T}>0, \tag{9-59}$$

and the isobaric potential itself acquires the minimum value $Z=Z_{min}$.

This rule finds wide application in some problems of molecular physics and physical chemistry.

Thus, both the isochoric-isothermal and the isobaric potentials determine the direction of a process in the system and fully characterize the conditions of equilibrium, and Eqs. (9-55)-(9-59) express the general conditions of system equilibrium.

The choice of the equation suitable for studying the equilibrium of a thermodynamic system depends on the parameters that characterize the system involved.

If

$$dQ=0, \quad \text{then } (\partial S)_{U,V}=0, \quad (\partial^2 S)_{U,V}<0, \quad S=S_{max};$$

if

$$S, V=\text{const}, \quad \text{then } (\partial U)_{V,S}=0, \quad (\partial^2 U)_{V,S}>0, \quad U=U_{min};$$

if

$$S, p=\text{const}, \quad \text{then } (\partial I)_{p,S}=0, \quad (\partial^2 I)_{p,S}>0, \quad I=I_{min};$$

if

$$T, V=\text{const}, \quad \text{then } (\partial F)_{V,T}=0, \quad (\partial^2 F)_{V,T}>0, \quad F=F_{min};$$

if

$$T, p=\text{const}, \quad \text{then } (\partial Z)_{p,T}=0; \quad (\partial^2 Z)_{p,T}>0, \quad Z=Z_{min}.$$

Thus, the conditions of equilibrium require that the thermodynamic potentials be minimum with their variables, and the entropy be maximum when the internal energy and volume of the system are constant.

9-6. The Equilibrium of a Homogeneous System

In the preceding section the conditions for stable equilibrium of a system were established, under which the temperature and pressure must be the same at all points of the system. In addition, any homogeneous system in a state of stable equilibrium must satisfy the following conditions:

$$(\partial p/\partial V)_T < 0; \quad C_V > 0.$$

It follows from the *first condition* that an increase in volume at constant temperature is always accompanied by a decrease in pressure. The contrary condition $[(\partial p/\partial V)_T > 0]$ is in violation with the condition of thermodynamic stability and cannot be realized.

The *second condition* requires without fail that C_V be greater than zero, $C_V > 0$, and, consequently, $C_p > 0$, i.e. that the heat capacity of the body C_V be positive, since otherwise (with $C_V < 0$) it would be possible to create a perpetual motion machine of the second kind, and this is impossible. It should be noted here that for all real bodies there exist a single equilibrium state in which the derivative $(\partial p/\partial V)_T$ turns into zero. This state is referred to as the *critical state.*

Stable equilibrium at the critical point requires that the first and second derivatives be equal to zero

$$(\partial p/\partial V)_T = 0, \quad (\partial^2 p/\partial V^2)_T = 0,$$

and the third derivative be less than zero, i.e. be negative

$$(\partial^3 p/\partial V^3)_T < 0.$$

9-7. Conditions of Equilibrium for Several Phases of a Substance

The equilibrium coexistence of several contracting phases of a substance that are capable of changing into one another is called *phase equilibrium.* Let us consider the equilibrium state of the system consisting of two phases of the same substance. In conditions of equilibrium $p_1 = p_2$ and $T_1 = T_2$. However, in contrast to a homogeneous body these conditions are insufficient for the equilibrium of a two-phase system either of whose of phases can change to the other. Equilibrium requires that the stability of the phases in the state of equilibrium be the same.

In accordance with Eq. (9-59), with $p = \text{const}$ and $T = \text{const}$, the isobaric potential Z of the system must have a minimum value, i.e. $dZ = 0$. But for a two-phase system $Z = m_1 z_1(p, T) + m_2 z_2(p, T)$. It follows from this that the condition of equilibrium must have the form $z_1(p,T)\, dm_1 + z_2(p,T)\, dm_2 = 0$. Since the quantity of the substance does not change: $m_1 + m_2 = m = \text{const}$, $dm_1 = -dm_2$, then $[z_1(p, T) - z_2(p, T)]\, dm_1 = 0$, but $dm_1 \neq 0$, therefore

$$z_1(p, T) = z_2(p, T),$$

which is precisely the *third condition* of phase equilibrium. This equation shows that for a two-phase system to be in equilibrium the temperatures,

pressures and chemical potentials must be the same. A change in the mass of the phases does not disturb equilibrium. Thus, two phases can be in equilibrium with each other, not at any values of p and T, but only at definite temperatures and pressures, with the magnitude of one of these parameters determining fully the value of the other parameter: $p=p(T)$.

9-8. Thermodynamic Diagrams

The p-T diagrams. Very often one encounters engineering problems requiring the investigation of processes in which substances change from solid to liquid, from solid to vapour and from liquid to vapour phase.

It has been shown experimentally that substances can exist in the solid, liquid and vapour (gaseous) states and, depending on pressure and temperature, exist simultaneously in two or three states.

The change of a substance from solid to liquid phase is called *fusion*, from solid to vapour—*sublimation*, and from liquid to vapour—*vaporization*. Reverse processes are referred to as *solidification*, or *crystallization*, desublimation and condensation.

The change from one phase to another is called the *change of phase* or *phase transition*. At a given pressure the substance changes from one phase to another at a definite temperature.

The equilibrium state of phases of the substance, capable of changing into one another, is called the *phase equilibrium*.

It is most convenient to represent graphically phase equilibrium on a p-T diagram where phase changes are depicted by points.

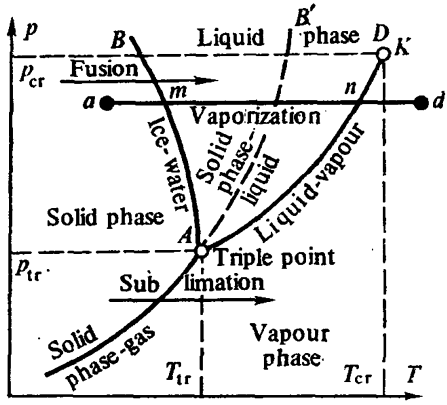


FIG. 9-3

If curves $p=p(T)$ are plotted on the p-T diagram, then the points of phase equilibrium are arranged on these curves and the entire diagram is referred to as a *phase diagram*. In addition to the p-T diagram, thermodynamics deals with p-v, T-s, i-T, i-s and other diagrams. The points lying on both sides of the phase curve on the p-T diagram correspond to the homogeneous states of the substance, i.e. to individual phases.

Shown in Fig. 9-3 is the phase p-T diagram of a substance. The curve AC corresponds to the equilibrium state of the solid and vapour phases, curve AB represents the equilibrium state of the liquid and solid phases, and curve AD—the equilibrium state of the liquid and vapour (gaseous) phases.

Arranged to the right of the curve CAD is the region of the vapour phase of the substance; between curves AB and AD—the region of the liquid

phase of the substance; to the left of the curve *CAD*—the region of the solid phase of the substance.

Curve *AD* represents on the phase diagram the dependence between pressure and temperature in the process of a change from the liquid to the vapour phase: $p=f(T_s)$. This curve terminates at the critical point *k*. At pressures exceeding that at the critical point there is no change from the liquid to the vapour phase, since at these pressures there is no difference between the liquid and vapour. If heat is rejected from the liquid at a pressure $p=\text{const}$ then, at a certain temperature, the liquid changes to the solid state. This temperature is called the solidification, or fusion, point T_f, and the amount of heat transferred from the liquid in the process is referred to as the *latent heat of fusion.* In the course of fusion a substance exists in two phases. On the diagram curve *AB* represents the dependence between pressure and temperature when there is a change of phase from solid to liquid $p=f(T_f)$.

In the isobaric process *a-d* the heating of a solid body is represented by line *a-m*. At the point *m* melting, or fusion, of the solid takes place. Heating of the liquid is depicted by line *m-n* at the end point of which vaporization of the liquid occurs (point *n*). Heating of the vapour (gas) is represented by the line of the process *n-d*. Thus, the heating processes *a-m*, *m-n*, *n-d* occur in a substance consisting of one phase, and the processes of fusion (point *m*) and vaporization (point *n*) are realized with the substance comprising two phases. The point *d* corresponds to the single-phase state of the substance or to superheated vapour. Upon a change in pressure the positions of points *m* and *n* shall change, as can be seen from Fig. 9-3.

If the pressure of the working medium is lower than the pressure at point *A*, the solid body turns directly into the vapour, by passing the liquid phase, i.e. the phenomenon of sublimation is observed.

Curve *AC* (sublimation curve) represents the dependence between pressure and temperature in the process of change of phase of a substance from solid to vapour $p=f(T_{subl})$. This change of phase, or phase transition, takes place at the expense of added heat, known as the *latent heat of sublimation.* The points lying on curve *AC* correspond to a two-phase system solid—vapour (for instance, saturated water vapour on top of the surface of ice).

At each point of any of the curves of phase equilibrium, *AB*, *AD* and *AC*, two phases are in equilibrium. The curves of phase equilibrium divide the plane of the *p-T* diagram into regions of the crystalline, liquid and vapour phases in which the substance exists fully in one phase. At the point of intersection of the three curves of phase equilibrium (point *A*) the three phases of substance, solid, liquid and vapour, coexist in equilibrium. Points at which all the three phases of a substance coexist in equilibrium are called the *triple points.* The pressure and temperature at the triple point can be determined analytically from the conditions of equilibrium for the three phases:

$$p_1=p_2=p_3=p; \quad t_1=t_2=t_3=t; \quad z_1=z_2=z_3.$$

Equilibrium coexistence of more than three phases of a substance (with the exception of solutions) is impossible.

At the triple point each substance has its proper definite properties. For instance, for water: $p_A=0.00611$ bar, $v_A=0.001$ m³/kg; $t_A=0.01$ °C.

The arrangement and shape of curves on the diagram depend on the nature of each substance and are established by experiment.

Figure 9-3 shows the *p-T* diagram of an anomalous substance, water, on which the change-of-phase lines *AB*, *AD* and *AC* are plotted. On this diagram the curve *AB* runs to the left—with an increase in pressure the change-of-phase (solidification) temperature diminishes. The anomal nature of water is treated in greater detail in special courses in thermodynamics and physics.

For "normal" pure substances the curve *AB* is inclined to the right (dotted line), indicating that with an increase in pressure the change-of-phase (solidification) temperature increases.

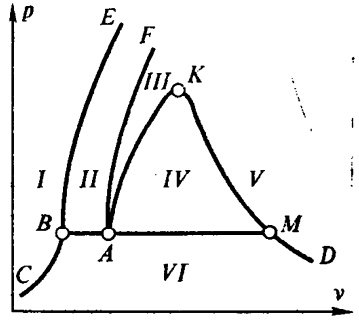


FIG. 9-4

The p-v diagram. In addition to the *p-T* diagram, the *p-v* diagram is of considerable interest.

Let us consider (without observing scales) the *p-v* diagram of a normal substance, on which the regions of phase equilibrium are represented by areas. A digram of this kind is illustrated in Fig. 9-4. On the diagram area *I* represents the solid phase, area *II* depicts a two-phase system consisting of liquid and solid phases, area *III* represents the liquid phase, area *IV* is the region of the liquid and vapour phases, area *V* is the region of the gaseous state of a body and area *VI* represents the region of the solid and vapour phases.

Curve *KD* determines the volume of dry saturated vapour, v'', and curve *AK*—the volume of boiling liquid, v', at different pressures; curve *AF* determines the volume of the liquid phase that is in equilibrium with the solid phase; curve *CE* determines the volume of the solid phase, and curve *BM* corresponds to the equilibrium of the three phases (or corresponds to the triple point on the *p-T* diagram). Point *k* is the critical point.

An investigation of the curves *Ak* and *Dk* makes it clear that with an increase in pressure and, consequently, in temperature the volume of the boiling liquid increases and the volume of the dry saturated vapour diminishes. At the critical point *k* the two volumes become equal. If the changes of phase from solid to liquid or vapour and from liquid to vapour proceed at a constant pressure, the temperature does not change in the process. The general form of the isotherms in the liquid- and vapour-phase region is presented in Fig. 4-3.

T-s diagram. In conducting the thermodynamic analysis of many processes and cycles encountered in practice, wide use is made of the *T-s* diagram

which makes it possible to observe the change of the temperature of the working medium and to find the quantity of heat involved in a particular process. What makes this diagram somewhat inconvenient to use is that when determining the quantity of heat, we have to measure corresponding areas.

On a *T-s* diagram the values of the specific entropy s are plotted on the abscissa, or x-axis, and absolute temperature T, on the y-axis.

Plotted on the *T-s* diagram are the curve of boiling liquid (the liquid boundary curve, or line) and the curve of dry saturated vapour (the vapour boundary line). In addition, the isobars, isochors, isenthalpies and the lines of constant degree of dryness are plotted on the diagram.

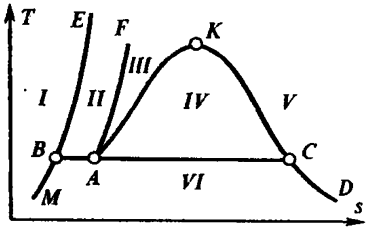


FIG. 9-5

The general appearance of the *T-s* diagram for a normal substance is represented in Fig. 9-5. On the liquid boundary line *Ak* lie the boiling liquid points, and on the vapour boundary line *Ck*—the points of dry saturated vapour. Region *I* pertains to the solid phase, region *II* represents the equilibrium coexistence of the solid and liquid phases, region *III*—the liquid phase, region *IV*—the equilibrium coexistence of the liquid and vapour phases, region *V* pertains to the vapour phase, and region *VI* depicts the equilibrium coexistence of the solid and vapour phases. Line *BC* determines the temperature at the triple point or the temperature of the equilibrium coexistence of all the three phases.

On the *T-s* diagram a reversible adiabatic or isentropic process is represented by a vertical straight line (s=const), and an isothermal process—by a horizontal straight line (T=const).

The general form of the isobars $p(s, T)$=const can be established by analyzing Eq. (6-45) $(\partial T/\partial s)_p = T/c_p$, in which the term $(\partial T/\partial s)_p$ is the slope of the isobars ($\tan \alpha$). The slope of the isobars is always positive, since the term $(\partial T/\partial s_p) > 0$. In the region of the two-phase state of substance the isobars coincide with the isotherms and are horizontal straight lines. In the vapour region of substance isobars are represented by curves rising from the left to the right with their convex side facing the abscissa. The higher the pressure, the higher the corresponding isobars.

In accordance with Eq. (6-45), the slope of an isochor $v(s, T)$=const is equal to $(\partial T/\partial s)_V = T/c_V$; since the term $(\partial T/\partial s)_V$ is always greater than zero, an isochor is a rising curve, steeper than an isobar. The slope of the isenthalpy $i(s, T)$=const $(\partial T/\partial s)_i$ is smaller than zero, therefore the isenthalpies are represented on the *T-s* diagram by descending lines.

9-9. Clausius-Clapeyron Equation

For two-phase systems the Clausius-Clapeyron equation can be derived on the basis of the second law of thermodynamics, applying the method of cyclic processes. Let us consider an elementary cyclic process, realized with a unit mass of substance, on the p-v diagram. Let the initial state of 1 kg of substance at pressure p be represented by point A with a specific volume v_1 (Fig. 9-6). During the process AB the latent heat of phase transition r is added at constant temperature T, resulting in the formation of vapour with specific volume v_2 at the point B. The process AB is simultaneously an isobaric and an isothermal one. From point B the vapour expands adiabatically along line BC with the pressure dropping by dp, and the temperature—by dT, and at the point C the temperature becomes equal to $T-dT$. From point C the vapour undergoes compression at a constant temperature $T-dT$ until point D. The process CD is simultaneously an isobaric and an isothermal one. From point D the vapour is compressed adiabatically to the initial state A. Together, these processes make up an elementary Carnot cycle.

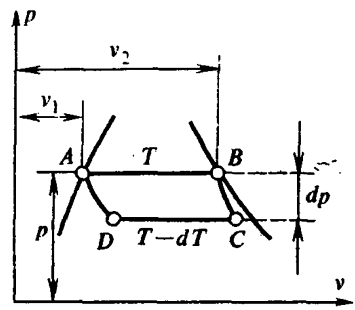


FIG. 9-6

The thermal efficiency of the Carnot cycle is found from the equation

$$\eta_t = l/q_1 = (T_1 - T_2)/T_1.$$

For the elementary Carnot cycle considered we obtain

$$T_1 = T; \quad T_2 = T - dT; \quad q_1 = r; \quad dl = dp(v_2 - v_1).$$

Then

$$\eta_t = dp\,\frac{v_2 - v_1}{r} = \frac{T - T + dT}{T} = \frac{dT}{T},$$

whence

$$v_2 - v_1 = \frac{r}{T} \cdot \frac{dT}{dp} \tag{9-60}$$

or

$$r = T(v_2 - v_1)\frac{dp}{dT} \tag{9-61}$$

Equation (9-61) is known as the *Clausius-Clapeyron equation.* It relates the thermal and caloric properties upon phase transition of substance. The quantity dp/dT is the derivative of pressure with respect to temperature taken on the change-of-phase boundary line. The difference between the specific volumes $v_2 - v_1$ can be positive as well as negative.

Clausius-Clapeyron equation is applicable to all changes in the state of aggregation of chemically homogeneous substances; to the fusion and sublimation of solids, to the transformation from one solid state to another, to the formation and fusion of crystals; it can also be used to determine the change in specific volume in the process of vaporization, to determine the full heat of vaporization. In addition, this equation in its general form characterizes the change in the pressure of phases in equilibrium depending on pressure, i.e. it pertains to the curves *AC*, *AB* and *AD* (Fig. 9-3). However, the physical meaning of the quantities in the equations is different for each individual case. For the case involving the evaporation of liquid (curve *AD*): r=the total heat of vaporization; v_1=specific volume of the boiling liquid; v_2=specific volume of dry saturated vapour. For the case involving the fusion (melting) of a solid (*AB*): n=specific heat of fusion; v_1=specific volume of the solid; v_2=specific volume of liquid. For a case of sublimation (*AC*): λ=specific heat of sublimation; v_1=specific volume of the solid; v_2=specific volume of dry saturated vapour.

For an overwhelming majority of substances the volume of the solid phase is less than the volume of the liquid phase and the volume of the vapour phase of all substances is considerably greater than the volume of the liquid phase. That is why the difference v_2-v_1 is almost always greater than zero.

For water, however due to its anomality, the volume of ice (of the solid phase) is greater than the volume of water (liquid phase) at the moment of phase transition, i.e. $v_2-v_1<0$. This, as it was already pointed out, explains the anomalous run of the curve representing the solidification of water on the *p-T* diagram. In fact, from Clausius-Clapeyron equation

$$dp/dT=r/T(v_2-v_1),$$

but since r and T are always positive and the difference v_2-v_1 is negative for water, then dp/dT will be smaller than zero. This means that the slope of the tangent to the solidification line on the *p-T* diagram shall be greater than 90°, i.e., with a rise in pressure the curve shall deflect to the left (to the side of lower temperatures). For normal liquids $v_2-v_1>0$, and, consequently, all phase-transition boundary lines (Fig. 9-3) shall incline to the right with rising pressure.

9-10. The Nernst Heat Theorem

Experimental investigations of the properties of various substances at extremely low temperatures led to the discovery of a new important regularity that was given the name of Nernst heat theorem.

The Nernst theorem does not stem from the first and second laws of thermodynamics, but it expresses a new law of nature, that is why the theorem is often referred to as the *third law of thermodynamics*. At present, this law can be derived from the basic concepts of quantum statistics.

Nernst theorem was first established while determining chemical affinity, but subsequently it turned out that it was of greater importance, than the solution of just this problem. A correct solution of the problem of chemical affinity was given by Van't Hoff who proved that chemical affinity should be measured not by the thermal effect, but by the decrease of the isobaric potential ΔZ, if a reaction proceeds at constant temperature and pressure, or by the decrease of the isochoric-isothermal potential ΔF, if substances enter a reaction at constant temperature and volume, since the decrease of the isochoric-isothermal potential in these conditions is precisely equal to the work done by the chemical forces: $\Delta F = L$, and the work L, being the measure of affinity, is determined by Gibbs-Helmholtz' equation

$$L = Q + T(\partial L/\partial T)_V .$$

Integration of this equation yields the thermodynamically indeterminable constant C that does not permit determination of the absolute magnitude of the work of affinity L.

We encounter the same difficulty in determining the absolute value of entropy.

Generalizing the experimental data obtained in investigating the properties of various substances at extremely low temperatures, Nernst has found that the difference $L-Q$ or $\Delta F-\Delta U=T(\partial \Delta F/\partial T)_V$ diminishes with dropping temperature and if the temperature tends to zero, $T\to 0$, the factor $(\partial \Delta F/\partial T)_V$ in the product $T(\partial \Delta F/\partial T)_V$ also tends to zero.

Hence, at $T\to 0$ the change of the isochoric-isothermal potential F_2-F_1 in equilibrium systems, undergoing isothermal processes, ceases to depend on temperature

$$\frac{\partial}{\partial T}(F_2-F_1)\to 0, \quad \text{or} \quad \lim_{T\to 0}\left[\frac{\partial}{\partial T}(\Delta F)\right]=0. \tag{9-62}$$

This proof is called the *Nernst heat theorem.*

Nernst conclusions make it possible to find from the Gibbs-Helmholtz equation that $L=Q$ at $T\to 0$ or $\Delta F=\Delta U$ at $T\to 0$.

The quantities ΔU and ΔF, Q and L are plotted as functions of T in Fig. 9-7*a* and *b*. It follows from Eq. (9-62) that for condensed systems the curves ΔU and ΔF or Q and L merge with each other at temperatures close to absolute zero, and this leads to the conclusion that for $T=0$ the curves have common tangents parallel with the T-axis.

From the differential equation of the isochoric-isothermal potential we find that $(\partial F/\partial T)_V=-S$, therefore, by considering Eq. (9-62), we obtain

$$S_2-S_1\to 0 \quad \text{or} \quad \lim_{T\to 0}\Delta S=0,$$

i.e. with $T\to 0$ isothermal processes occur without a change of entropy, and the entropy of the body in an equilibrium state ceases to be a function of state

$$\lim_{T\to 0}(\partial S/\partial p)_T=\lim_{T\to 0}(\partial S/\partial V)_T=0.$$

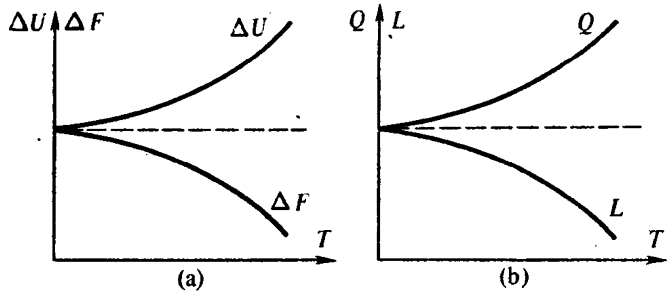


FIG. 9-7

At absolute zero the isothermal process is also an isentropic (adiabatic) process.

The Nernst principle was developed by Planck who suggested that at absolute zero temperature the entropy of all homogeneous crystalline (condensed) substances in a state of equilibrium becomes zero.

$$S_0=0. \tag{9-63}$$

This equality is considered to be the third law of thermodynamics.

The fact that entropy is equal to zero at $T\to 0$ is associated with the quantum nature of real systems that are in a state of stable and not semi-stable equilibrium at a temperature $T=0$ K.

It follows from the condition $S_0=0$ that

$$\lim_{T\to 0}(\partial Z/\partial T)_p=\lim_{T\to 0}(\partial F/\partial T)_V=0. \tag{9-64}$$

Equation (9-64) is also an expression of Nernst heat theorem.

On the basis of Planck hypothesis it is possible to determine the entropy and enthalpy of a system in an arbitrary state of equilibrium by the known heat capacity. For instance, for a homogeneous system of a constant composition

$$S(p, T)=\int_0^T c_p\frac{dT}{T};\quad I(p, T)=\int_0^T c_p dT+I_0,$$

where integration is based on the assumption that $p=$const.

The heat capacity c_p is taken at the given pressure p; I is the value of enthalpy at $T=0$ K.

The corollaries of the Nernst heat theorem are of great practical importance. Let us consider some of them.

Thermal coefficients at $T\to 0$. The thermal expansion coefficient α_t and the coefficient of thermal pressure γ_t are equal to

$$\alpha_t=\frac{1}{v}\left(\frac{\partial V}{\partial T}\right)_p;\quad \gamma_t=\frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v.$$

But from equation (9-29) it follows that

$$(\partial v/\partial T)_p = -(\partial s/\partial p)_T,$$

and from equation (9-29)

$$(\partial p/\partial T)_v = (\partial s/\partial v)_T,$$

therefore

$$\alpha_t = -\frac{1}{v}\left(\frac{\partial s}{\partial p}\right)_T \quad \text{and} \quad \gamma_t = \frac{1}{p}\left(\frac{\partial s}{\partial v}\right)_T$$

It follows from Nernst theorem that at $T \to 0$ entropy does not change, i.e. is independent of p and v, therefore with $T \to 0$

$$\alpha_t \to 0 \quad \text{and} \quad \gamma_t \to 0$$

or the coefficient of thermal expansion and the coefficient of thermal pressure become zero with $T \to 0$.

Heat capacities c_p and c_v at $T \to 0$. Due to the fact that the derivatives $(\partial s/\partial T)_v$ and $(\partial s/\partial T)_p$ are equal to zero at $T \to 0$ [Eq. (6-45)], the heat capacities c_p and c_v also become zero near the temperature of absolute zero, i.e. $c_v \to 0$ and $c_p \to 0$ with $T \to 0$.

Unattainability of absolute zero temperature. Considering cyclic processes, Nernst arrived at the conclusion that there exists no cyclic process of finite dimensions in the course of which a body would cool to absolute zero temperature. This reasoning led Nernst to the conclusion that absolute zero temperature is unattainable.

Let us consider the Carnot cycle in which the temperature of the source is $T_1 = T$ and the temperature of the sink is $T_2 = 0$ (Fig. 9-8).

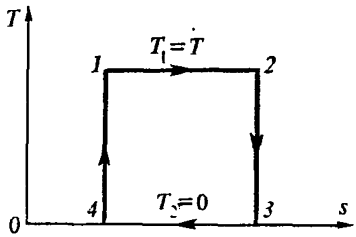


FIG. 9-8

According to the second law of thermodynamics, for a cyclic process $\oint dQ/T = 0$ or $\Delta s_{12} + \Delta s_{23} + \Delta s_{34} + \Delta s_{41} = 0$, where $\Delta s_{12} = Q/T$; $\Delta s_{23} = 0$ (adiabatic process); $\Delta s_{34} = 0$, $\Delta s_{41} = 0$ (adiabatic process).

Hence, it follows that the realization of such a cycle which makes it possible to obtain continuously the work at the expense of cooling of one source results in the possibility of creating a perpetual motion machine of the second kind which, in accordance with the second law of thermodynamics, is impossible. Therefore, absolute zero temperature is unattainable. However, the possibility of obtaining temperatures as close to absolute zero as desirable is not precluded.

Typical Questions and Examples to Chapter Nine

1. What does a thermodynamic identity express?
2. What are the peculiarities of thermodynamic functions?
3. Which thermodynamic functions are considered as basic?
4. Which independent variables determine each of the basic thermodynamic functions?
5. What is meant by the isochoric-isothermal potential and the bound energy?
6. The physical meaning of the isochoric-isothermal potential.
7. What quantities make up the total energy of a system?
8. The Gibbs-Helmholtz equation of maximum work at constant TV and Tp.
9. What quantities are referred to as thermodynamic potentials?
10. What is meant by the chemical potential?
11. Name the classes of thermodynamic systems.
12. Phase changes of the first and second kind.
13. What state is said to be stable, labile, metastable?
14. What conditions should be realized for stable equilibrium of the thermodynamic system?
15. Conditions of equilibrium for a homogeneous system.
16. Conditions of equilibrium for several phases of a substance.
17. p-T diagram.
18. p-V diagram.
19. T-s diagram.
20. The Clausius-Clapeyron equation and its derivation.
21. Nernst heat theorem.

Example 9-1. Prove that for an ideal gas

$$(\partial F/\partial T)_p = -S - R \quad \text{and} \quad (\partial F/\partial p)_T = -V.$$

When p and T are independent variables the characteristic function is the isobaric-isothermal potential Z

$$Z = U - TS + pV = F + pV \quad \text{or} \quad F = Z - pV.$$

Differentiating the last equation with respect to T at constant pressure, we obtain

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial Z}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p.$$

From Clapeyron equation we find that

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \quad \text{and} \quad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{RT}{p^2}.$$

Taking into account Eq. (9-25) and Clapeyron equation, we obtain

$$\left(\frac{\partial F}{\partial T}\right)_p = -S - p\left(\frac{R}{p}\right) = -S - R.$$

Differentiating the potential Z with respect to p at constant temperature, we find

$$\left(\frac{\partial F}{\partial p}\right)_T = \left(\frac{\partial Z}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T - V$$

and with account taken of Eq. (9-25) and Clapeyron equation, we get

$$\left(\frac{\partial F}{\partial p}\right)_T = V - V - V = -V.$$

Example 9-2. Determine the quantities L, Q, ΔI, ΔU, ΔS, ΔF and ΔZ for 1 kmole of an ideal gas expanding isothermally from $p_1 = 1.0$ to $p_2 = 0.5$ bar at temperature of 1000 K.

The work upon isothermal expansion

$$L = 1000 \times 8314.2 \times 2.3 \log 1/0.5 = 5730 \text{ kJ/mole.}$$

The heat added in the process $Q = L = 5730$ kJ/mole.
The change of enthalpy $\Delta I = 0$.
The change of entropy

$$\Delta S = \frac{Q}{T} = \frac{5730}{1000} = 5.73 \text{ kJ/kmole K.}$$

The change of internal energy $\Delta U = 0$.
The isochoric-isothermal potential $\Delta F = -L_{max} = -5730$ kJ/kmole.
The isobaric potential $\Delta Z = L_{max} = 5730$ kJ/kmole.

Example 9-3. Determine the maximum work done by 1 m³ of air at pressure $p_1 = 100$ bar and temperature $T_1 = 300$ K; the pressure of the surrounding medium $p_0 = 1$ bar and temperature $T_0 = 300$ K.

The maximum specific work is determined by Eq. (8-26)

$$l_{max} = (u_1 - u_2) - T_0(s_1 - s_2) + p_0(v_1 - v_2)$$

or

$$l_{max} = c_v(T_1 - T_0) - T_0(c_p \ln T_1/T_0 - R \ln p_1/p_0) + Rp_0(T_1/p_1 - T_0/p_0),$$

$$l_{max} = 300 \times 0.287 \times 2.3 \log 100 + 0.287[(300/100) - 300] = 311 \text{ kJ/kg.}$$

The mass of air

$$m = (p_1V_1)/(RT_1) = (100 \times 10^5)/(287 \times 300) = 116 \text{ kg;}$$

$$L_{max} = 311 \times 116 = 36\,100 \text{ kJ.}$$

Example 9-4. Prove the following relationships:

$$U = Z - T(\partial Z/\partial T)_p - p(\partial Z/\partial p)_T;$$

$$C_V = -T(\partial^2 F/\partial T^2)_V; \quad C_p = -T(\partial^2 Z/\partial T^2)_p;$$

$$(\partial U/\partial V)_S = (\partial F/\partial V)_T; \quad (\partial I/\partial p)_S = (\partial Z/\partial p)_T;$$

$$(\partial F/\partial T)_V = (\partial Z/\partial T)_p; \quad (\partial F/\partial V)_T = (\partial U/\partial V)_S.$$

CHAPTER TEN

DIFFERENTIAL EQUATIONS OF THERMODYNAMICS

10-1. Basic Partial Differential Equations of Thermodynamics

The first and second laws of thermodynamics make it possible to determine for any working medium the relation between its parameters in the differential form. Hence, if some of the parameters are determined by experiment, the others can be determined by integrating corresponding differential equations. The way in which these differential equations are worked out shall be presented below.

Since the derivatives of characteristic functions determine the physical properties of substances, the differential equations express the quantitative links between the various physical properties of substance, stemming from the first and second laws of thermodynamics.

In our investigations we shall start with the mathematical expressions, or equations, of the first and second laws of thermodynamics and the thermodynamic identities: (5-8), (5-9), (5-13), (6-39), (6-46) and (6-47).

With $p=\text{const}$ Eq. (6-45) acquires the form

$$C_p=T(\partial S/\partial T)_p. \tag{10-1}$$

For an isochoric process

$$C_V=T(\partial S/\partial T)_V \tag{10-2}$$

i.e. at $V=\text{const}$, the heat capacity C_V is equal to the product of absolute temperature T and the partial derivative of entropy S with respect to temperature T.

At different independent variables determining the internal energy dU the differential equation of the first law of thermodynamics $dQ=dU+p\,dV$ is expressed as follows.

With independent variables V and T through Eq. (6-4′)

$$dQ=\left(\frac{\partial U}{\partial T}\right)_V dT+\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right]dV.$$

With independent variables p and V

$$dQ=\left(\frac{\partial U}{\partial p}\right)_V dp+\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right]dV. \tag{10-3}$$

With independent variables p and T. Substituting into the equation of the

first law of thermodynamics the values of dU and dV from Eqs. (5-3) and (4-7) with the same independent variables, we obtain

$$dQ=\left(\frac{\partial U}{\partial T}\right)_p dT+\left(\frac{\partial U}{\partial p}\right)_T dp+p\left[\left(\frac{\partial V}{\partial T}\right)_p dT+\left(\frac{\partial V}{\partial p}\right)_T\right] dp,$$

or

$$dQ=\left[\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p\right] dT+\left[\left(\frac{\partial U}{\partial p}\right)_T+p\left(\frac{\partial V}{\partial p}\right)_T\right] dp. \tag{10-4}$$

The partial derivative of internal energy is $\left(\frac{\partial U}{\partial V}\right)_T$. Substituting into the basic equation for the change of entropy S, $dS=dQ/T$, the value of dQ from Eq. (6-4'), we obtain

$$dS=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT+\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right] dV.$$

Comparing the derived equation with Eq. (6-40), we find that

$$\left(\frac{\partial S}{\partial T}\right)_V=\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \tag{10-5}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right]. \tag{10-6}$$

To eliminate the variable S, we take the second partial derivatives: of Eq. (10-5) with respect to V at $T=\text{const}$ and of Eq. (10-6) with repect to T at $V=\text{const}$;

$$\frac{\partial^2 S}{\partial T\,\partial V}=\frac{1}{T}\cdot\frac{\partial^2 U}{\partial T\,\partial V}$$

and

$$\frac{\partial^2 S}{\partial V\,\partial T}=\frac{1}{T}\left[\frac{\partial^2 U}{\partial V\,\partial T}+\left(\frac{\partial p}{\partial T}\right)_V\right]-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right].$$

The obtained derivatives are equal to each other

$$\frac{1}{T}\cdot\frac{\partial^2 U}{\partial T\,\partial V}=\frac{1}{T}\left[\frac{\partial^2 U}{\partial V\,\partial T}+\left(\frac{\partial p}{\partial T}\right)_V\right]-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right],$$

whence

$$\left(\frac{\partial p}{\partial T}\right)_V=\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T+p\right]$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p. \tag{10-7}$$

The partial derivative of internal energy $(\partial U/\partial p)_T$. Let us substitute in the main equation of entropy, $dS=dQ/T$, the value of dQ from Eq. (10-4), then

$$dS=\frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p\right]dT+\frac{1}{T}\left[\left(\frac{\partial U}{\partial p}\right)_T+p\left(\frac{\partial V}{\partial p}\right)_T\right]dp.$$

On the basis of the properties of the coefficients of a total differential we find from the last equation and Eq. (6-40) that

$$\left(\frac{\partial S}{\partial T}\right)_p=\frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p\right]; \tag{10-8}$$

$$\left(\frac{\partial S}{\partial p}\right)_T=\frac{1}{T}\left[\left(\frac{\partial U}{\partial p}\right)_T+p\left(\frac{\partial V}{\partial p}\right)_T\right]. \tag{10-9}$$

To eliminate the variable S, we take the second partial derivatives in Eq. (10-8) with repect to p at $T=\text{const}$, and in Eq. (10-8) with respect to T at $p=\text{const}$ and, equating the right-hand sides, we obtain

$$\frac{1}{T}\left[\frac{\partial^2 U}{\partial p\,\partial T}+\left(\frac{\partial U}{\partial T}\right)_p+p\frac{\partial^2 V}{\partial p\,\partial T}\right]=-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial p}\right)_T+p\left(\frac{\partial V}{\partial p}\right)_T\right]+\frac{1}{T}\left[\frac{\partial^2 U}{\partial T\,\partial p}+p\frac{\partial^2 V}{\partial T\,\partial p}\right],$$

whence

$$\left(\frac{\partial U}{\partial p}\right)_T=-\left[T\left(\frac{\partial V}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial p}\right)_T\right]. \tag{10-10}$$

Partial derivative of internal energy $(\partial U/\partial T)_p$. For an isobaric process taking place with independent variables p and T the partial differential equation of the first law of thermodynamics takes the form

$$dQ_p=\left[\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p\right]dT_p$$

and

$$\frac{dQ_p}{dT_p}=C_p=\left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p,$$

whence

$$\left(\frac{\partial U}{\partial T}\right)_p=C_p-p\left(\frac{\partial V}{\partial T}\right)_p. \tag{10-11}$$

With independent variables V and T the differential equation of heat shall be similar to Eq. (6-14)

$$dQ=T\left(\frac{\partial p}{\partial T}\right)_V dV+C_V\,dT. \tag{10-12}$$

Differential equation of heat with independent variables p and T. When p and T are independent variables the differential equation of the first law of thermodynamics is obtained from Eq. (10-4).

Substituting into Eq. (10-4) Eqs. (10-11) and (10-10), we find that

$$dQ=\left[C_p-p\left(\frac{\partial V}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p dT\right]+\left[-T\left(\frac{\partial V}{\partial T}\right)_p-p\left(\frac{\partial V}{\partial p}\right)_T+p\left(\frac{\partial V}{\partial p}\right)_T\right]dp. \tag{10-13}$$

Upon transformations we obtain

$$dQ=C_p\,dT-T\left(\frac{\partial V}{\partial T}\right)_p dp. \tag{10-14}$$

Differential equations of enthalpy and entropy with independent variables p and T.

Comparing equations (5-21) and (6-47) we obtain

$$dS=\left(\frac{\partial I}{\partial T}\right)_p\frac{dT}{T}+\frac{1}{T}\left[\left(\frac{\partial I}{\partial p}\right)_T-V\right]dp. \tag{10-15}$$

The partial derivatives of entropy are found by comparing the coefficients of identical equations.

Comparing Eq. (10-15) with the identical Eq. (6-40), we get

$$\left(\frac{\partial S}{\partial T}\right)_p=\frac{1}{T}\left(\frac{\partial I}{\partial T}\right)_p; \tag{10-16}$$

$$\left(\frac{\partial S}{\partial p}\right)_T=\frac{1}{T}\left[\left(\frac{\partial I}{\partial p}\right)-V\right]. \tag{10-17}$$

To eliminate entropy S, we take the second derivatives in Eq. (10-16) with respect to p at $T=\text{const}$ and in Eq. (10-17) with respect to T with $p=\text{const}$

$$\frac{\partial^2 S}{\partial T\,\partial p}=\frac{1}{T}\frac{\partial^2 I}{\partial T\,\partial p};$$

$$\frac{\partial^2 S}{\partial p\,\partial T}=\frac{1}{T}\left[\frac{\partial^2 I}{\partial p\,\partial T}-\left(\frac{\partial V}{\partial T}\right)_p\right]-\frac{1}{T^2}\left[\left(\frac{\partial I}{\partial p}\right)_T-V\right].$$

The derivatives obtained are equal to each other, therefore

$$\left(\frac{\partial V}{\partial T}\right)_p=-\frac{1}{T}\left[\left(\frac{\partial I}{\partial p}\right)_T-V\right], \tag{10-18}$$

whence

$$\left(\frac{\partial I}{\partial p}\right)_T=V-T\left(\frac{\partial V}{\partial T}\right)_p. \tag{10-19}$$

Eq. (10-19) is used to analyze isothermal processes. Substituting in Eq. (5-21) for enthalpy the quantity $(\partial I/\partial p)_T$ from Eq. (10-19) and the value $(\partial I/\partial T)_p$ from Eq. (6-12), we obtain

$$dI=C_p\,dT-\left[T\left(\frac{\partial V}{\partial T}\right)_p-V\right]dp. \tag{10-20}$$

Substituting in Eq. (6-40) for entropy the quantity $(\partial S/\partial T)_p$ from Eq. (10-1) and $(\partial S/\partial p)_T$ from Eq. (9-29), we get

$$dS=\left(\frac{C_p}{T}\right)dT-\left(\frac{\partial V}{\partial T}\right)_p dp. \tag{10-21}$$

Equations (6-46) and (6-47) permit calculation of the important partial derivatives of entropy

$$\left(\frac{\partial U}{\partial S}\right)_V=T; \quad \left(\frac{\partial S}{\partial V}\right)_U=\frac{p}{T};$$

$$\left(\frac{\partial I}{\partial S}\right)_p=T; \quad \left(\frac{\partial S}{\partial p}\right)_I=-\frac{V}{T};$$

$$\left(\frac{\partial U}{\partial V}\right)_S=-p; \quad \left(\frac{\partial I}{\partial p}\right)_S=V.$$

The differential equations relating the constant-pressure and constant-volume heat capacities are of great importance in thermodynamics. Let us find the dependence of heat capacity C_p on pressure, and of heat capacity C_V on volume at constant temperature.

Let us take in Eq. (10-1) the second derivative with respect to p at $T=$ const

$$\frac{\partial^2 S}{\partial T\,\partial p}=\frac{1}{T}\left(\frac{\partial C_p}{\partial p}\right)_T.$$

In equation (9-29) we take the second derivative with respect to T at $p=$ $=$ constant

$$\frac{\partial^2 S}{\partial p\,\partial T}=-\left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

The second partial derivatives obtained are equal, therefore

$$\left(\frac{\partial C_p}{\partial p}\right)_T=-T\left(\frac{\partial^2 V}{\partial T^2}\right)_p. \tag{10-22}$$

This equation is used to derive the thermal equation of state of a real gas, $p=f(V, T)$, if the dependence of heat capacity C_p on parameters is determined by experiment. For this purpose it is necessary to integrate two times Eq. (10-22) and determine the values of the integration constants.

The same method is applied to derive the equation for C_V.

In Eq. (10-2) we take the second derivative with respect to V with $T=$ const

$$\frac{\partial^2 S}{\partial T\,\partial V}=\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T.$$

Differentiating again two times Eq. (9-20) with respect to T with $V=$ const, we find that

$$\frac{\partial^2 S}{\partial V\,\partial T}=\left(\frac{\partial^2 p}{\partial T^2}\right)_V.$$

The second partial derivatives are equal to each other

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V. \tag{10-23}$$

Eq. (10-23) determines the dependence of C_V on volume.

Important formulae, expressed in terms of partial derivatives, that can be used to determine the heat capacities C_p and C_V may be derived from Eqs. (10-1) and (10-2). Transforming Eq. (10-1), we obtain

$$C_p = T\left(\frac{\partial S}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p.$$

Applying Maxwell's relation, Eq. (9-12), we get

$$C_p = T\left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial V}{\partial T}\right)_p. \tag{10-24}$$

Transforming Eq. (10-2), $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$, we obtain

$$C_V = T\left(\frac{\partial S}{\partial p}\right)_V \left(\frac{\partial p}{\partial T}\right)_V.$$

Applying Maxwell's relation (Eq. 9-8), we get

$$C_V = -T\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial p}{\partial T}\right)_V. \tag{10-25}$$

Differentiating the expression for enthalpy, $I = U + pV$, with respect to V at $T = \text{const}$, we obtain

$$\left(\frac{\partial I}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p + V\left(\frac{\partial p}{\partial V}\right)_T.$$

Using Eq. (10-7), we get

$$\left(\frac{\partial I}{\partial T}\right)_V = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T. \tag{10-26}$$

By analogy, differentiating the expressions for enthalpy I with respect to T at $V = \text{const}$, we obtain

$$\left(\frac{\partial I}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial T}\right)_V,$$

or, applying Eq. (6-5), we have

$$\left(\frac{\partial I}{\partial T}\right)_V = C_V + V\left(\frac{\partial p}{\partial T}\right)_V. \tag{10-27}$$

Equations (10-6), (10-10), (10-11), (10-19), (10-20), (10-22), (10-23), (10-26) and (10-27) relate thermal and caloric quantities and are widely used in practice as calculation formulae for the thermal properties of

substances once the caloric properties have been determined by experiment. In addition, Eq. (10-22) is widely applied to determine the dependence of V on T, if heat capacity C_p is measured experimentally.

The differential equations of the isochoric-isothermal and isobaric potentials are treated in Chapter 9.

10-2. Application of Differential Equations to the Solution of Some Problems in Thermodynamics

1. The heat capacities C_p and C_V of an ideal gas are independent of pressure and volume at $T=\text{const}$.

It follows from Eq. (10-22) that

$$(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p.$$

Differentiating the equation of state at $p=\text{const}$, we obtain

$$(\partial V/\partial T)_p = mR/p.$$

The second derivative of the partial derivative is

$$(\partial^2 V/\partial T^2)_p = 0,$$

therefore

$$(\partial C_p/\partial p)_T = 0.$$

At constant temperature the heat capacity C_p of an ideal gas does not depend on pressure.

From Eq. (10-23) it follows that

$$(\partial C_V/\partial V)_T = T(\partial^2 p/\partial T^2)_V.$$

Differentiating the equation of state at $V=\text{const}$, we obtain

$$(\partial p/\partial T)_V = mR/V.$$

The second derivative of the above derivative is equal to

$$(\partial^2 p/\partial T^2)_V = 0,$$

therefore

$$(\partial C_V/\partial V)_T = 0$$

The isochoric (constant-volume) heat capacity C_V of an ideal gas does not depend on volume and, consequently, on pressure.

2. According to Joule's law, the internal energy of an ideal gas only depends on temperature and is independent of volume and pressure. This assumption demands that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial U}{\partial p}\right)_T = 0.$$

From the equation of state we obtain

$$\left(\frac{\partial p}{\partial T}\right)_V=\frac{mR}{V};\quad \left(\frac{\partial V}{\partial T}\right)_p=\frac{mR}{p};\quad \left(\frac{\partial V}{\partial p}\right)_T=-\frac{mRT}{p^2}.$$

Substituting into Eq. (10-7) the value of $\left(\frac{\partial p}{\partial T}\right)_V$, we find

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p=T\left(\frac{mR}{V}\right)-p=0.$$

Substituting into Eq. (10-10) the values of $\left(\frac{\partial V}{\partial T}\right)_p$ and $\left(\frac{\partial V}{\partial p}\right)_T$, we get

$$\left(\frac{\partial U}{\partial p}\right)_T=-\left[T\left(\frac{\partial V}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial p}\right)_T\right]=-\left[T\left(\frac{mR}{p}\right)-p\left(\frac{mRT}{p^2}\right)\right]=0.$$

For an ideal gas

$$\left(\frac{\partial U}{\partial T}\right)_V=\frac{dU}{dT}=C_V.$$

3. Determine the internal energy of a gas obeying the van der Waals equation. From van der Waals equation we obtain

$$p=\frac{RT}{(v-b)}-\left(\frac{a}{v^2}\right)\quad\text{and}\quad\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{(v-b)}.$$

Substituting into Eq. (10-12) the value of derivative, we find that

$$dU=\left[T\left(\frac{\partial p}{\partial T}\right)_v-p\right]dv+c_v\,dT$$

and

$$dU=\left[\frac{TR}{(v-b)}\right]dv-p\,dv+c_v\,dT.$$

Substituting the value of p into the derived equation, we get

$$dU=\left[\frac{TR}{(v-b)}\right]dv-\left[\frac{RT}{(v-b)}\right]dv-\left(\frac{a}{v^2}\right)dv+c_v\,dT=c_v\,dT-\left(\frac{a}{v^2}\right)dv.$$

4. Prove that on the T-s diagram the convex side of an isochor faces the abscissa.

To solve the problem it must be shown that the second derivative

$(\partial^2T/\partial s^2)_v>0$.

At $v=\text{const}$ it follows from Eq. (6-46) that

$du_v=T\,ds_v$.

Taking into account Eq. (6-5) we have

$c_v=(\partial U/\partial T)_v=T(\partial s/\partial T)_v$,

whence

$$(\partial T/\partial s)_v = T/c_v.$$

Take the second derivative on condition that $c_v = \text{const}$,

$$\left(\frac{\partial^2 T}{\partial s^2}\right)_v = \frac{\partial}{\partial s}\left[\left(\frac{\partial T}{\partial s}\right)_v\right]_v = \frac{\partial}{\partial s}\left(\frac{T}{c_v}\right)_v = \frac{1}{c_v}\left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{c_v^2}.$$

Heat capacity at constant-volume $c_v > 0$ and $T > 0$, whence the second derivative $(\partial^2 T/\partial s^2)_v$ is also greater than zero, $(\partial^2 T/\partial s^2)_v > 0$.

Hence, on the T-s diagram the convex side of an isochor faces the abscissa or x-axis.

5. Making use of the partial differential equations for the coefficients of isothermal and adiabatic compression, prove that an adiabat runs steeper than an isotherm.

Dividing Eq. (10-14) by Eq. (10-13), assuming $dQ = 0$ and $ds = 0$, we find that

$$-\frac{c_p\left(\frac{\partial p}{\partial T}\right)_v}{c_v\left(\frac{\partial v}{\partial T}\right)_p} = \left(\frac{\partial p}{\partial v}\right)_s.$$

Substituting the value of $\left(\frac{\partial p}{\partial T}\right)_v$ from Eq. (4-8), we obtain

$$\left(\frac{\partial p}{\partial v}\right)_s = \frac{c_p\left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_p}{c_v\left(\frac{\partial v}{\partial T}\right)_p},$$

whence

$$\left(\frac{\partial p}{\partial v}\right)_s = k\left(\frac{\partial p}{\partial v}\right)_T.$$

The coefficient of adiabatic expansion β_s is k times larger than the coefficient of isothermal expansion β_T

$$\beta_s = k\beta_T.$$

It follows from this that the adiabat t runs steeper than the isotherm.

6. Prove that

$$c_p - c_v = \left[\left(\frac{\partial u}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p.$$

Taking into account Eq. (6-16), the quantity c_p can be expressed by the following relationship

$$c_p = c_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p,$$

and from Eq. (10-7) it follows that

$$T=\frac{\left(\frac{\partial u}{\partial v}\right)_T+p}{\left(\frac{\partial p}{\partial T}\right)_v}.$$

Substituting into the above equation the value of T, we have

$$c_p=c_v+\frac{\left(\frac{\partial u}{\partial v}\right)_T+p}{\left(\frac{\partial p}{\partial T}\right)_v}\left[\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p\right],$$

whence

$$c_p=c_v+\left(\frac{\partial u}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p+p\left(\frac{\partial v}{\partial T}\right)_p$$

or

$$c_p-c_v=\left[\left(\frac{\partial u}{\partial v}\right)_T+p\right]\left(\frac{\partial v}{\partial T}\right)_p\Big],$$

where the term $p\left(\frac{\partial v}{\partial T}\right)_p$ represents external work obtained due to a change in temperature by 1 K, and the term $\left(\frac{\partial u}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$ expresses the change in internal energy with temperature rising by 1 K at constant pressure.

7. Use Eqs. (6-46) and (10-13) to prove that

$(\partial T/\partial v)_u=[p-T(\partial p/\partial T)_v]/c_v$.

Comparing Eqs. (6-46) and (10-13), we obtain

$du=T\,ds-p\,dv$; $ds=(c_v\,dT)/T+(\partial p/\partial T)_v\,dv$;

$du=c_v\,dT+T(\partial p/\partial T)_v\,dv-p\,dv$;

$du=c_v\,dT+[T(\partial p/\partial T)_v-p]\,dv$,

whence, at $u=$const

$(\partial T/\partial v)_u=[p-T(\partial p/\partial T)_v]/c_v$.

8. Use Eqs. (10-2) and (9-20) to prove that

$(\partial T/\partial v)_s-T(p/c_v)\gamma_t$,

where γ_t is coefficient of thermal pressure, determined by Eq. (4-11).

The main partial derivatives of T, v and s are interrelated as follows

$$\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial v}{\partial s}\right)_T\left(\frac{\partial s}{\partial T}\right)_v=-1.$$

Therefore,

$$\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial v}{\partial T}\right)_T\left(\frac{c_v}{T}\right)=-1,$$

or

$$\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{T}{c_v}\right)\left(\frac{\partial p}{\partial T}\right)_v=-\left(\frac{T}{c_v}\right)\left(\frac{p}{p}\right)\left(\frac{\partial p}{\partial T}\right)_v,$$

whence

$$\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{Tp}{c_v}\right)\gamma_t.$$

9. Prove that

$$\left(\frac{\partial T}{\partial p}\right)_v\left(\frac{\partial s}{\partial v}\right)_p-\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial s}{\partial p}\right)_v=1;$$

$$\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial v}{\partial s}\right)_T-\left(\frac{\partial p}{\partial s}\right)_T\left(\frac{\partial v}{\partial T}\right)_s=1.$$

Substituting the values of c_p and c_v from Eqs. (10-1) and (10-2) into Eq. (6-16), we obtain

$$T\left(\frac{\partial s}{\partial T}\right)_p-T\left(\frac{\partial s}{\partial T}\right)_v=T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

or

$$\left(\frac{\partial s}{\partial T}\right)_p-\left(\frac{\partial s}{\partial T}\right)_v=\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p,$$

whence

$$\left(\frac{\partial s}{\partial v}\right)_p\left(\frac{\partial T}{\partial p}\right)_v-\left(\frac{\partial s}{\partial p}\right)_v\left(\frac{\partial T}{\partial v}\right)_p=1.$$

Replacing in the above equation T with p and p with T, and also v with s and s with v, we obtain

$$\left(\frac{\partial v}{\partial s}\right)_T\left(\frac{\partial p}{\partial T}\right)_s-\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial p}{\partial s}\right)_T=1.$$

10. Prove that

$$c_p-c_v=T\frac{(\partial^2F/\partial T\,\partial V)^2}{(\partial^2F/\partial v^2)_T}.$$

Equation (6-16) can be presented in the following form

$$c_p-c_v=T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p=T\frac{(\partial p/\partial T)_v}{(\partial T/\partial v)_p}=T\frac{(\partial p/\partial T)_v^2}{(\partial T/\partial v)_p(\partial p/\partial T)_v}.$$

Using the relation between the parameters of state, Eq. (4-8), we obtain the identity

$$(\partial v/\partial p)_T (\partial T/\partial v)_p (\partial p/\partial T)_v = -1.$$

Substituting the obtained expression into Eq. (6-16), we get

$$c_p - c_v = -T \frac{(\partial p/\partial T)_v^2}{(\partial p/\partial v)_T}.$$

But from Eq. (9-17)

$$p = -\left(\frac{\partial F}{\partial v}\right)_T \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial^2 F}{\partial T \partial v}\right);$$

$$\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial^2 F}{\partial v^2}\right)_T,$$

therefore

$$c_p - c_v = T \frac{(\partial^2 F/\partial T \partial v)^2}{(\partial^2 F/\partial v^2)_T}.$$

11. Show that $c_p - c_v = -T(ds/dv)_T (\partial s/\partial p)_T$. According to Eq. (6-16),

$$c_p - c_v = T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p.$$

It follows from Eq. (6-20) that

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T,$$

and from Eq. (9-29)

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T,$$

therefore

$$c_p - c_v = -T \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial s}{\partial p}\right)_T.$$

12. Determine the thermodynamic functions for independent variables p, I and T, F.

Let us take Eq. (6-47)

$$T\,ds = dI - V\,dp.$$

With independent variables p and I the thermodynamic function is entropy $S(p, I)$

$$dS = \frac{dI}{T} - \left(\frac{V}{T}\right) dp.$$

At constant pressure

$$T=\left(\frac{dI}{dS}\right)_p=\frac{1}{\left(\frac{\partial S}{\partial I}\right)_p}$$

and

$$V=-\left(\frac{\partial S}{\partial p}\right)_I\left(\frac{\partial I}{\partial S}\right)_p=-\frac{\left(\frac{\partial S}{\partial p}\right)_I}{\left(\frac{\partial S}{\partial I}\right)_p}.$$

Let us write down Eq. (9-15)

$$dF=-S\,dT-p\,dV.$$

With independent variables T and F the thermodynamic function is volume $V(T, F)$

$$dV=-\frac{dF}{p}-\left(\frac{S}{p}\right)dT.$$

At constant temperature

$$p=-\left(\frac{\partial F}{\partial V}\right)_T=-\frac{1}{\left(\frac{\partial V}{\partial F}\right)_T}$$

and

$$S=T\left(\frac{\partial V}{\partial T}\right)_F=\frac{\left(\frac{\partial V}{\partial T}\right)_F}{\left(\frac{\partial V}{\partial F}\right)_T}.$$

CHAPTER ELEVEN

WATER VAPOUR (STEAM)

11-1. Basic Definitions

The vapours of various substances, water, ammonia, carbon dioxide and others, have found wide application in all fields of industrial production. Of all these, water vapour, or steam, is most widely applied as a working medium in steam turbines, steam engines, in atomic power plants and also as a heat-carrying agent in various heat-exchange apparatus, etc.

The process involving a change from the liquid to the vapour phase is called *vaporization. By evaporation* is meant vaporization, always taking place at any temperature from the free surface of liquid or solid. The process of evaporation consists in that the individual molecules, moving at great velocities, overcome the attraction of neighbouring molecules and escape into the surrounding space. The intensity, or rate, of evaporation increases with rising temperature of the liquid.

The process of boiling consists in that, if heat is added to a liquid, then at some temperature, depending on the physical properties of the working medium and pressure, vaporization sets in both from the free surface of the liquid and inside it.

The conversion of a substance from vapour (gas) into liquid or solid is referred to as *condensation.* The process of condensation, just as the process of vaporization, proceeds at constant temperature, if the pressure does not change in the process. The liquid resulting from the condensation of vapour is called *condensate.*

The process involving the transition of a solid directly into a vapour is called *sublimation.* The reverse process of conversion of a vapour into a solid is referred to as *desublimation.*

If vaporization of a liquid takes place in an infinite space, all the liquid may convert into vapour. But, if vaporization occurs in a closed vessel, the molecules escaping from the liquid fill the free space on top of it, with a fraction of the molecules, moving in the vapour space on top of the surface, returning back into the liquid. At a certain moment of time the number of molecules escaping from the liquid may become equal to the number of molecules returning back into it. At that moment a maximum possible number of molecules shall fill the space on top of the liquid. In this state the vapour acquires a maximum density at a given temperature and is referred to as *saturated vapour.*

Thus, the vapour that is in contact with the liquid and is in thermal equilibrium with it is called saturated vapour. With a change in liquid

temperature the equilibrium is disturbed, causing a corresponding change in the density and pressure of the saturated vapour.

Saturated vapour that is free of suspended highly-dispersed (finest) particles of the liquid phase is called *dry saturated vapour*. The state of dry saturated vapour is determined by one parameter: pressure, or specific volume, or temperature.

Saturated vapour that contains suspended highly-dispersed particles of the liquid phase, evenly distributed over the entire mass of vapour, is called *wet saturated vapour*.

The mass fraction of dry saturated vapour in wet is called the *degree of dryness* and denoted by the letter x

$$x=\frac{\text{mass of dry saturated vapour in wet}}{\text{mass of wet vapour}}.$$

The mass fraction of the boiling liquid in wet vapour, equal to $(1-x)$, is referred to as the *degree of humidity*. For a liquid boiling at the saturation temperature $x=0$, and for dry saturated vapour $x=1$, consequently, the degree of dryness, or the dryness fraction, may change only from 0 to 1. It is clear that the state of wet vapour is determined by two quantities: temperature or pressure and some other parameter, e.g. the degree of dryness.

If a certain amount of heat is added to dry saturated vapour at a constant pressure, the temperature of the vapour shall rise, and the resulting vapour is referred to as superheated vapour. At a given pressure superheated vapour has a higher temperature than dry saturated vapour. Superheated vapour cannot be produced on top of the surface of liquid. The temperature of superheated vapour as well as of a gas is a function of volume and pressure.

Superheated vapour is not saturated, since at a given pressure the specific volume of superheated vapour is greater than the specific volume of dry saturated vapour, and the density is smaller. In its physical properties the superheated vapour approaches a gas and is closer to it, the greater the degree of superheating.

11-2. Peculiarities of the *p-v* Diagram of Water Vapour (Steam)

The *p-v* diagram of the system consisting of liquid and vapour is a graphical representation of the dependence of the specific volumes of water and vapour (steam) on pressure.

Let 1 kg of water, at a temperature of 0 °C and a pressure p, occupy a volume v_0 (line *NS* in Fig. 11-1). The curve *AE* represents the dependence of the specific volume of water on pressure at $t=0$ °C. Since water is almost incompressible, curve *AE* runs almost parallel to the ordinates. If heat is added to water at a constant pressure, its temperature shall rise and the specific volume increase. At some temperature t_s water begins to boil and at the point A' its specific volume v' reaches its maximum value at the given

pressure. With rising pressure the temperature of the boiling liquid, t_s, and the volume v' also increase.

The dependence of the specific volume v' on pressure is represented in Fig. 11-1 by curve AK referred to as the *liquid boundary line* (or curve). Curve AK is characterized by the degree of dryness $x=0$.

If heat is continually added to the liquid at a constant pressure, the process of vaporization will initiate, the amount of water shall decrease and the quantity of vapour shall increase.

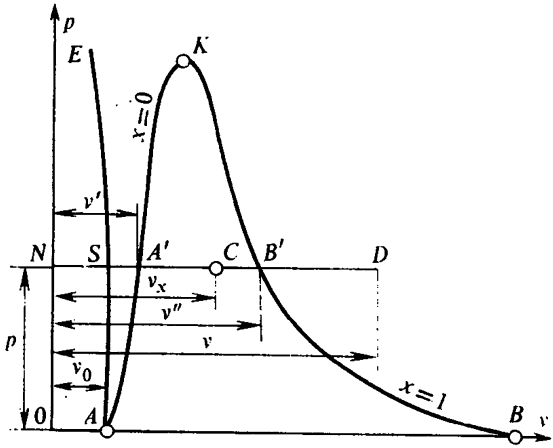


FIG. 11-1

At the moment vaporization terminates at point B' the vapour shall be dry and saturated. The specific volume of dry saturated vapour is denoted by v''.

If vaporization proceeds at a constant pressure, its temperature does not change and the process $A'B'$ is simultaneously an isobaric and isothermal one. At points A' and B' the substance is in a single phase. At intermediate points the substance consists of a mixture of water and vapour. Such a mixture is called a *two-phase system.*

The dependence of the specific volume v'' on pressure is represented in Fig. 11-1 by curve KB, referred to as the *vapour boundary line.* The curve KB is characterized by the degree of dryness $x=1$.

Point A corresponds to the state of boiling liquid at the triple point ($t_0=0.01°\approx 0$ °C), and the isobar AB corresponds to the states of equilibrium of the three phases (triple point on the p-T diagram). With the scale chosen for the graphical presentation, this isobar almost coincides with the abscissa.

If heat is added to dry saturated vapour at a constant pressure, then its temperature and volume shall increase and the dry saturated vapour shall convert into superheated (point D).

The two curves AK and BK divide the diagram into three parts. To the left of the liquid boundary curve AK to the zero isotherm is the liquid

region. The two-phase system, consisting of a mixture of water and vapour, lies between the curves *AK* and *BK*. To the right of the curve *BK*, up to the point *K*, is the region of superheated vapour. The two curves *AK* and *BK* merge at point *K*, referred to as the *critical point.*

The critical point is the final point of the liquid-to-vapour change of phase, initiating at the triple point.

Above the critical point a substance cannot exist in a two-phase state. No pressure can enable a gas to liquefy at temperatures above the critical.

For water the parameters of the critical point are $t_{cr}=374.12$ °C; $v_{cr}=0.003\ 147$ m³/kg; $p_{cr}=221.15$ bar; $i_{cr}=2095.2$ kJ/kg; $s_{cr}=4.424$ kJ/kg·deg.

The region confined between the isotherm of water at 0 °C (line *AE*) and the ordinates is the region of equilibrium coexistence of the liquid and solid phases.

11-3. Main Parameters of Liquid and Dry Saturated Vapours. Heat of Vaporization

At a temperature of 0 °C and various pressures the specific volume of water can be assumed equal to be approximately $v_0\approx 0.001$ m³/kg. With rising pressure and, hence, temperature the specific volume of boiling liquid increases and at high pressures it differs considerably from the volume at 0 °C. For instance, at $p=50$ bar $v'=0.001\ 285\ 9$ m³/kg, at $p=220$ bar $v'=0.002\ 69$ m³/kg.

The amount of heat spent to heat water from a temperature of 0 °C to the boiling point at corresponding pressures is determined by equation

$$q=i'-i'_0 \qquad (11\text{-}1)$$

where i' = enthalpy of the boiling liquid;
i'_0 = enthalpy of water at 0 °C.

In thermodynamics, in the state corresponding to the triple point, the enthalpy and entropy of water are assumed to be zero:

$$s'_0=0; \quad i'_0=0.$$

At the triple point the internal energy of water $u'_0=i'_0-p_0v'_0$, but since $i'_0=0$, then $u'_0=-p_0v'_0$, whence $u'_0=-0.006\ 11\times 0.001\times 10^5=-0.611$ J/kg which is a very small quantity; it may therefore be assumed that at 0 °C the internal energy of liquid $u'_0\approx 0$.

The enthalpy of boiling liquid is determined by the pressure or temperature from Steam Tables.

The internal energy of boiling liquid, u', is determined from the general formula for enthalpy

$$i=u+pv \quad \text{or} \quad u'=i'-pv'. \qquad (11\text{-}2)$$

When heat is continually added to water heated to the boiling point at a given pressure, vaporization of the water initiates. In the process of vaporization the temperature shall remain constant, till the last drop of

liquid converts into steam. In this final state dry saturated steam is obtained.

The quantity of heat spent to convert 1 kg of water at the boiling point into steam is called the *heat of vaporization* and denoted by the letter r. The heat of vaporization r is fully determined by pressure or temperature. With rising temperature and pressure r decreases and becomes equal to zero at the critical point. The heat of vaporization r is spent to change the internal potential energy or to perform work of disintegration ϱ and external work of expansion $p(v''-v')=\psi$. The quantity ϱ is called the *internal* and ψ—the *external heat of vaporization.* The heat of vaporization is equal to

$$r=\varrho+p(v''-v')=\varrho+\psi. \tag{11-3}$$

The enthalpy of dry saturated steam i'' is determined by the formula

$$i''=i'+r. \tag{11-4}$$

The internal energy of dry saturated steam

$$u''=i''-pv''. \tag{11-5}$$

Dry saturated steam is characterized by one parameter of state, pressure or temperature.

The values of i'', i', r, v'', v' are taken from Steam Tables. At the critical point the enthalpy of dry saturated steam is equal to the enthalpy of the liquid (water).

11-4. Main Properties of Wet Saturated Steam

In steam boilers only wet steam of a greater or smaller dryness fraction, or quality, is generated in the space above the surface of evaporation. Wet steam is characterized by pressure p or temperature t_s and by the degree of dryness x. The temperature of wet steam is equal to the boiling point of the liquid at the given pressure. The specific volume of wet steam v_x is determined as the volume of a mixture of dry steam and water

$$v_x=v''x+(1-x)v'. \tag{11-6}$$

The degree of dryness of steam generated in boilers reaches 0.9-0.96, therefore, for low pressures, the value of the volume of water $(1-x)v'$ can be neglected and the volume of the wet steam is found by the approximate formula

$$v_x\approx v''x. \tag{11-7}$$

The enthalpy of wet steam, i_x, is determined by formula

$$i_x=i'+rx, \tag{11-8}$$

where i' = enthalpy of water;

rx = quantity of heat spent to evaporate an x fraction of water.

The internal energy of wet steam

$$u_x=i_x-pv_x. \tag{11-9}$$

11-5. Main Properties of Superheated Steam

Steam is called *superheated* if at a given pressure, it has a temperature higher than that of saturated steam. Superheated steam is produced in a special apparatus, superheater, from wet steam when a certain amount of heat is added to it. The *heat of superheating* is defined as the quantity of heat which is to be expended to superheat 1 kg of dry steam to a required temperature at a constant pressure.

In the superheater, wet steam first converts into dry, then into superheated steam. The pressure in the superheater is assumed to be constant and equal to boiler pressure (in reality pressure drops slightly across the superheater).

In modern practice, in boiler plants the temperature of superheated steam ranges from 550 to 600 °C. The temperature of superheated steam is not a function of pressure and can differ, but it cannot be lower than the temperature of dry steam at the given pressure. The properties of superheated vapours approach the properties of gases.

The amount of heat added to dry steam in the process of superheating can be determined from the equation

$$q_s = \int_{t_s}^{t} c_p\, dt \quad \text{or} \quad q_s = c_{pm}\Big|_{t_s}^{t} (t - t_s), \tag{11-10}$$

where c_p = true heat capacity of superheated steam at constant pressure;
c_{pm} = average heat capacity of superheated steam in the temperature interval from t_s to t.

Since the heat of superheating q_s, transferred to steam at a constant pressure, is expended only to change its enthalpy, the enthalpy of superheated steam is determined by the general equation

$$i = i' + r + c_{pm} \int_{t_s}^{t} dt. \tag{11-11}$$

The internal energy of superheated steam is equal to

$$u = i - pv, \tag{11-12}$$

where v is the specific volume of superheated steam.

The values of enthalpy, entropy and specific volume of superheated steam are taken from Steam Tables.

11-6. Entropy of Water and Steam

For reversible processes the main equation for the change of entropy is $ds = dq/T$.

For water $dq = c_{pf}\, dT$ and $ds = c_{pf} - dT/T$. At variable pressure the mass heat capacity of water can be assumed in the first approximation to be

constant, equal to $c_{pf}=4.19$ kJ/kg·dg. Therefore, integrating the last equation between the limits of 273.16 K and the boiling point of water T_s and assuming the entropy of water to be close to zero at the temperature 273.16 K and at all pressures, we obtain an approximate equation for the entropy of water at the boiling point

$$s'=\int_{273.16}^{T_s}\frac{dq}{T}=\int_{273.16}^{T_s}c_{pf}\frac{dT}{T}\approx c_{pf}\ln\frac{T_s}{273.16}. \tag{11-13}$$

Exact values of entropy s' are given in Tables I, II of the Appendix.

The change of entropy of water in an isobaric process is presented on the T-s diagram by the line s' (in process AB), shown in Fig. 11-2. The area

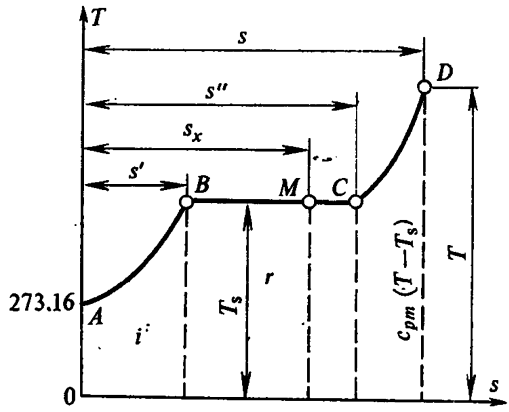


FIG. 11-2

below the curve of the process AB shall represent to some scale and with a slight error the enthalpy of boiling water i'.

After water is heated to the boiling point vaporization initiates at a constant pressure and constant temperature T_s. The amount of heat transferred to the water during the process of vaporization, equal to r, is represented on the T-s diagram by the area under the curve BC $(s''-s')T_s=r$. The entropy of dry steam s'' is determined by the formula

$$s''-s'=r/T_s \quad \text{or} \quad s''=s'+r/T_s. \tag{11-14}$$

Point C represents the end of vaporization or the state of dry saturated steam. If vaporization terminates yielding wet steam with a dryness fraction, or quality, x, point M, for instance, then the quantity of heat shall be represented by the smaller area $(s_x-s')T_s=rx$. The entropy of wet steam s_x is found by formula

$$s_x-s'=rx/T_s \quad \text{or} \quad s_x=s'+rx/T_s. \tag{11-15}$$

At a given pressure the degree of dryness of wet steam can be found from the ratio

$$x=BM/BC=(s_x-s')/(s''-s').$$

When steam is superheated from saturation temperature T_s to T the change of entropy is found from equation

$$s-s''=\int_{T_s}^{T}\frac{dq}{T}=\int_{T_s}^{T}\frac{di}{T},$$

where s = entropy of superheated steam;
T = temperature of superheated steam;
dq = superheat;
di = elementary change of enthalpy during superheating.

The change of entropy in the process of steam superheating is represented graphically by the curve CD. The area below that curve represents the heat of superheating $i-i''$.

The entropy of superheated steam is found from equation

$$s=s'+\frac{r}{T_s}+\int_{T_s}^{T}\frac{di}{T}. \qquad (11\text{-}16)$$

In practice, the entropy of water, dry and superheated steam is taken from Steam tables.

11-7. The *T-s* Diagram for Steam

On the *T-s* diagram an arbitrary process of heating a liquid, vaporization and superheating of steam at a constant pressure is depicted graphically by curve $AA_1'B_1''D_1$ (Fig. 11-3). Plotting on the diagram a number of such isobaric processes and connecting the characteristic points, we obtain the boundary lines for the boiling liquid AK ($x=0$), and dry vapour, KB ($x=1$) that merge at the critical point. The isobar plotted on the diagram corresponds to the pressure at the critical point, where $p_0=0.006\,11$ bar.

The liquid boundary line originates at the axis of ordinates at a temperature of 273.16 K, since, by definition, the entropy of liquid at the triple point is equal to zero. It should be noted that due to the anomality of water (maximum density at +4 °C), the isobars of the liquid have a complex structure near point A, but this, however, tells but little on practical calculations. Therefore, for the sake of simplicity, in Fig. 11-3 the isobars are plotted in the liquid region as for a normal liquid.

The boundary curves (lines) divide the diagram into three parts: to the left of line AK is the liquid region, between the lines AK and KB—the vapour region, and to the right of line KB up to point K—the region of superheated steam. In the liquid region the process of heating 1 kg of water from the

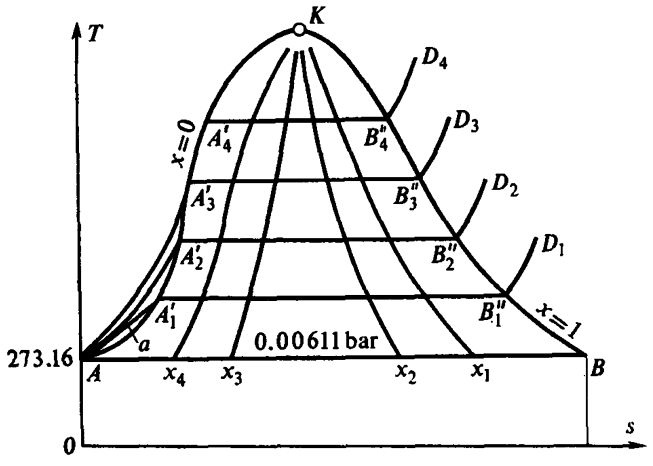


FIG. 11-3

temperature 0 °C to the boiling point proceeds along the isobar AaA'_1 that merges practically with the liquid boundary line.

Plotted on the diagram are isobars, lines of constant specific volume, and in the vapour region—the lines of constant degrees of dryness; in this region the isobars are straight lines running parallel to the abscissa, and in the region of superheated steam the isobars are resented by the curves *BD*. The region of the diagram below the isobar of the triple point, represents various states of the "vapour+ice" mixture.

On the *T-s* diagram the area confined between the line of a reversible process and the abscissa represents the quantity of heat added to 1 kg of the working medium, equal to $q = \int T\,ds$. The work output of any reversible cycle, equal to $l = q_1 - q_2$, is represented on the *T-s* diagram by the area of the cycle. The *T-s* diagram facilitates the determination of the efficiency of a reversible cycle.

That is why in engineering practice the *T-s* diagram is extensively employed in the investigation of thermodynamic processes and cycles, since it permits observation of the change in the temperature of the working medium and makes it possible to find the quantity of heat involved in a process. A slight drawback of this diagram consists in the necessity of measuring corresponding areas which hampers determination of the quantities of interest.

11-8. Steam Tables

The properties of superheated steam and to a greater extent of saturated steam differ from those of ideal gases.

The equations of state of vapours are rather complicated and are not used in calculations. As a result, tables and diagrams compiled and plotted on the basis of experimental and theoretical data are used in practice.

The most up-to-date tables and diagrams for steam were worked out at the Moscow Power Institute under the supervision of Professor M. P. Vukalovich [4]. The tables are compiled with a high degree of accuracy for superheated and saturated steam at temperatures up to 1000 °C and a pressure of 980 bar.

The tables for saturated steam contain data of the saturation temperature, pressure, specific volumes, enthalpy and entropy of water and dry steam, data on the latent heat of vaporization. The tables for superheated steam contain for different pressures and temperatures the values of the following main properties: specific volume, enthalpy and entropy.

Abbreviated Steam Tables I and II for saturated steam are given in the Appendix.

11-9. The *i-s* Diagram for Steam

The *i-s* diagram for steam was first suggested by Mollier in 1904, and it is usually referred to as the Mollier diagram. This diagram possesses certain merits over the *T*-s diagram when used for calculations.

The great advantage of the *i-s* diagram consists in that mechanical work and the amount of heat involved in processes are represented on the diagram by straight lines, and not by areas as is the case on the *T-s* diagram.

The diagram is constructed as follows: the enthalpy of steam is plotted on the axis of ordinates and entropy—on the abscissa. The origin of coordinates is assumed to be the state of water at the triple point, where $s'_0=0$, $i'_0=0$. Making use of the data taken from the Steam Tables, the liquid and vapour boundary lines, merging at the critical point K, are first plotted on the diagram. The liquid boundary line initiates at the origin of coordinates, since at that point enthalpy and entropy are assumed to be equal to zero (Fig. 11-4). The state of water is depicted by points on corresponding isobars which practically merge with the liquid boundary line. In the wet steam regions the isobars are straight inclined lines diverging in a fan-like manner from the liquid boundary line. In an isobaric process

$$ds=\frac{dq_p}{T}=\frac{di}{T}, \quad \text{or} \quad \left(\frac{\partial i}{\partial s}\right)_p=T.$$

The slope of the isobar with respect to the abscissa at each point of the diagram is equal numerically to the absolute temperature of the given state. Since in the wet steam region the isobar coincides with the isotherm, then, in accordance with the above equation, the isobars of wet steam are straight lines: $di=T_s\,ds$, and this is precisely the equation of a straight line.

In the region of superheated steam the isobars are represented by curves whose convex side faces downwards. The isobar *AB*, plotted on the *i-s* diagram, corresponds to the pressure at the triple point, $p_0=0.006\,11$ bar

In the wet steam region is plotted the network of lines of constant dryness fraction ($x=\text{const}$) that merge at the critical point *K*. In the wet steam region the constant-temperature lines, isotherms, coincide with the constant-

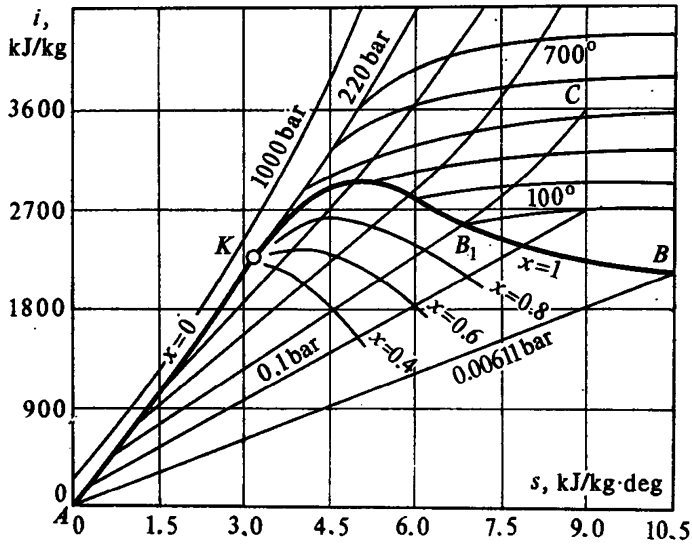


FIG. 11-4

pressure lines, isobars. In the superheated steam region the lines diverge: the isobars run upwards and the isotherms in this region are curves whose convex side faces upwards. At low pressures the isotherms are very close to horizontal lines; with an increase in pressure the curvature of the isotherms increases. Plotted on the *i-s* diagram is a network of isochors (constant-volume lines) that rise more steeply upwards, compared with the isobars.

A reversible adiabatic process is represented on the *i-s* diagram by a vertical straight line. Therefore, on the *i-s* diagram all vertical lines are adiabats. The region of diagram lying below the isobar of the triple point represents different states of the "vapour-ice" mixture.

At the present time, heat processes involving steam are investigated and studied with the aid of the *i-s* diagram and Steam tables, since they greatly simplify calculations.

Usually, the entire *i-s* diagram is not plotted, but only its upper part and that makes it possible to draw the diagram to a larger scale.

The *i-s* diagram for steam plotted on the data provided by Professor M. P. Vukalovich is given in the Appendix.

Typical Questions and Examples to Chapter Eleven

1. What is meant by boiling, vaporization and evaporation?
2. What process is referred to as sublimation and desublimation?
3. What kind of steam is called wet saturated, dry saturated and superheated?

4. What is meant by the degree of dryness, or dryness fraction, and by the degree of wetness?
5. Draw the p-v diagram for water vapour.
6. What points lie on the liquid and vapour boundary lines?
7. What are the parameters, or properties, of the critical point?
8. Under what conditions does the process of vaporization occur?
9. What is meant by the heat of vaporization and how is it determined?
10. How are the enthalpy and internal energy of dry saturated steam calculated?
11. Define the specific volume, enthalpy and internal energy of wet steam.
12. How are the enthalpy and internal energy of superheated steam calculated?
13. Entropy of water, wet, dry and superheated steam.
14. T-s diagram for steam.
15. Steam tables and their importance.
16. i-s diagram for steam.

Example 11-1. Determine the properties of wet saturated steam at a pressure of 20 bar and a dryness fraction $x=0.9$.

From the Steam tables or the i-s diagram we find the properties of boiling water or dry saturated steam at 20 bar

$t_s=212.37$ °C; $r=1890.7$ kJ/kg; $v'=0.0011768$ m³/kg;

$v''=0.09961$ m³/kg; $i'=908.6$ kJ/kg; $i''=2799.2$ kJ/kg;

$s'=2.4471$ kJ/kg·deg; $s''=6.3411$ kJ/kg·deg.

These data are used to find the parameters of wet steam

$$v_x=v'(1-x)+v''x=0.0011768\times0.1+0.09961\times0.9=0.08977 \text{ m}^3/\text{kg};$$

$$i_x=i'+rx=908.6+1890.7\times0.9=2610.2 \text{ kJ/kg};$$

$$\varrho_x=\frac{1}{v_x}=\frac{1}{0.08977}=11.16 \text{ kg/m}^3;$$

$$s_x=s'+\frac{rx}{T_s}=2.4471+\frac{1890.7\times0.9}{485.52}=5.949 \text{ kJ/kg·deg}.$$

Example 11-2. Determine the state of steam assuming: (1) $p=10$ bar and $v=0.17$ m³/kg; (2) $p=12$ bar and $t=200$ °C.

1. With $p=10$ bar the volume of dry steam $v''=0.1945$ m³/kg, therefore steam with a volume $v=0.17$ m³/kg will be wet steam with a dryness fraction

$$x\approx\frac{v}{v''}=\frac{0.17}{0.1945}=0.875.$$

2. With $p=12$ bar the temperature of saturated steam is $t_s=187.95$ °C, then, since steam temperature $t=200$ °C is higher than the saturation temperature, it is clear that the steam is superheated.

Example 11-3. Determine the state of steam at a pressure of 15 bar, if to generate the steam from water at a temperature of 0 °C 2400 kJ/kg of heat was spent.

Since at a pressure of 15 bar the enthalpy of steam is $i''=2791.8$ kJ/kg, let us assume the enthalpy of the generated steam to be equal to $i=2400$ kJ/kg (assuming that at 0 °C $i_0=0$). The generated steam shall be wet since $i''>2400$ kJ/kg.

The dryness fraction, or degree of dryness, is determined from equation $i_x=i'+rx$, using Table II in the Appendix.

$$x=(i_x-i')/r=(2400-844.5)/1947.3=0.798.$$

Example 11-4. Determine the mass and enthalpy of 0.5 m³ of wet steam with a degree of wetness equal to 10 per cent and a pressure of 10 bar. The specific volume of the steam

$$v_x\approx v''x\approx 0.1945(1-0.1)\approx 0.175 \text{ m}^3/\text{kg}.$$

The mass of the steam

$$m=\frac{V}{v_x}=\frac{0.5}{0.175}=2.9 \text{ kg}.$$

The enthalpy of the steam

$$i_x=m(i'+rx)=2.9(762.4+2015.3\times 0.9)=7520 \text{ kJ}.$$

Example 11-5. Determine the amount of heat spent in a superheater per 1 kg of steam, if the inlet parameters are: $p_1=80$ bar and $x_1=0.95$; the outlet parameters: $p_2=80$ bar and $t=500$ °C.

The enthalpy of the wet steam

$$i_x=i'+rx=1317.3+1441.2\times 0.95=2684.2 \text{ kJ/kg}$$

The amount of heat spent in the superheater

$$q=i-i_x=3405-2684.2=720.8 \text{ kJ/kg}.$$

The specific volume of wet steam

$$v_x\approx v''x\approx 0.02352\times 0.95=0.0223 \text{ m}^3/\text{kg}.$$

CHAPTER TWELVE

MAIN THERMODYNAMIC PROCESSES OF STEAM

12-1. General Investigation Method for Thermodynamic Steam Processes

Problems associated with the thermodynamic processes occurring in the regions of saturated and superheated steams can be solved either with the aid of Steam tables, or by means of the *i-s* diagram. In problems of this kind we usually determine: the initial and final conditions (parameters) of steam, the change in internal energy, enthalpy and entropy, the dryness fraction, the work and quantity of heat involved in a process.

When Steam tables are used to calculate processes of steam all the initial data required, and also the parameters of steam in the final state are taken from tables accounting of the conditions in which the process occurs (v=const, p=const, etc.). The parameters of wet steam then are calculated on the basis of the table data, applying the formulas given in Chapter XI.

The calculation method based on the use of Steam tables is the most accurate and it is used in applications where reliable values are to be obtained. However, with this method, additional time must be spent to find the required quantities from the tables and carry out the calculations.

Simpler and more vivid, but less exact, is the graphical calculation method with the aid of the *i-s* diagram. It is suitable for all steam processes, both in the region of saturated and superheated steam. This method permits to observe the change in the state of aggregation of steam in any process without resorting to formulae. The purely graphical calculation method is often used to check whether problems are correctly solved with the aid of tables.

The general calculation method with the aid of the *i-s* diagram consists in the following. The known parameters are used to plot on the diagram the initial state of steam. The line of the process is drawn and the parameters of the steam at the final point are determined.

The change in internal energy is calculated by the general equation derived for all processes

$$\Delta u = u_2 - u_1 = (i_2 - p_2 v_2) - (i_1 - p_1 v_1). \tag{12-1}$$

The amount of heat is calculated in an isochoric (constant-volume) process

$$q_v = u_2 - u_1 = (i_2 - p_2 v_2) - (i_1 - p_1 v_1) = i_2 - i_1 - v(p_2 - p_1); \tag{12-2}$$

in an isobaric (constant-pressure) process

$$q_p = i_2 - i_1; \tag{12-3}$$

in an isothermal (constant-temperature) process

$$q_T = T(s_2 - s_1). \tag{12-4}$$

External work (work on the surrounding medium) is calculated by the general equation for all processes

$$l = q - \Delta u. \tag{12-5}$$

12-2. Thermodynamic Processes Involving a Change of State of Steam

Isochoric Process. In an isochoric process, when heat is transferred to wet steam its pressure and temperature increase. With $v = \text{const}$ the dryness fraction may both decrease and increase with falling temperature. If the initial state of the substance is close to the curve $x = 0$, then, upon a decrease of temperature at $v = \text{const}$, the dryness fraction increases. If the initial state of the substance is close to the curve $x = 1$ then, upon a decrease of temperature at $v = \text{const}$, the degree of dryness diminishes.

In the isochoric process the external work is equal to zero. The added heat is expended to change the internal energy of the working medium

$$u_2 - u_1 = i_2 - i_1 - v(p_2 - p_1).$$

If the specific volume v of the process is less than the volume of dry saturated steam v'' in the final state, $v < v''$, then at the end of the process, the steam shall be wet; if $v > v''$, the steam shall be superheated.

The dryness fraction of wet steam can be determined by formula

$$v_x = (1 - x)v' + v''x,$$

whence

$$x = (v_x - v')/(v'' - v'). \tag{12-6}$$

On the p-v diagram the isochoric process is represented by a straight line running parallel with the axis of ordinates (Fig. 12-1*a*), and on the T-s diagram the process is depicted by a curve (Fig. 12-1*b*). In the wet

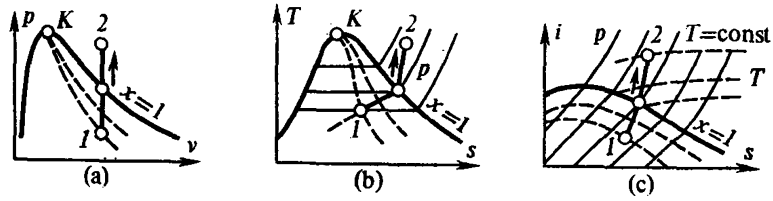


FIG. 12-1

steam region the isochor is directed with its convex side facing upward, and in the superheated steam region the convex side of the isochor faces downward. On the i-s diagram the isochor is represented by a curve whose convex side faces downward (Fig. 12-1*c*).

Isobaric Process. On the *i-s* diagram, in the saturated steam region, the isobaric process is represented by a straight line intersecting the liquid and vapour boundary lines. When heat is added to wet steam its dryness fraction increases and the steam (at a constant temperature) converts into dry steam, and if the addition of heat is continued, into superheated steam. In the superheated steam region the isobaric process is represented by the curve whose convex side is facing downward (Fig. 12-2*a*).

On the *p-v* diagram the isobaric process is represented by a horizontal straight line that depicts in the wet steam region not only the isobaric, but also the isothermal process (Fig. 12-2*b*). On the *T-s* diagram, in the wet

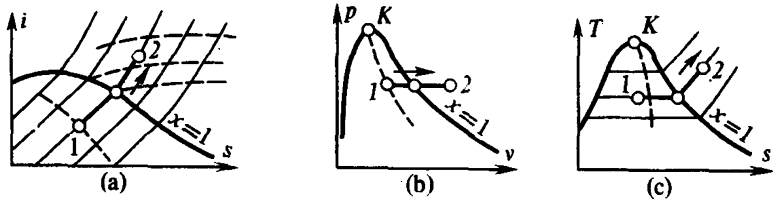


FIG. 12-2

steam region, the isobar is a straight horizontal line, and in the superheated steam region the process is represented by a curve whose convex side faces downward (Fig. 12-2*c*). The values of all quantities required for calculations are taken from saturated steam and superheated steam tables.

The change of the internal energy of steam

$$\Delta u = u_2 - u_1 = i_2 - i_1 - p(v_2 - v_1);$$

external work (done on the surrounding medium)

$$l = p(v_2 - v_1) = q - \Delta u;$$

and the quantity of added heat

$$q = i_2 - i_1.$$

When the quantity q is given and the problem is to determine the parameters of a second point lying in the region of two-phase states, use is made of the formula for the enthalpy of wet steam

$$i_2 = i'_2 + r_2 x_2, \qquad (12\text{-}7)$$

whence the dryness factor x_2 is determined and, knowing the latter, it is easy to find the other parameters.

Isothermal Process. On the *i-s* diagram, in the wet steam region, the isotherm coincides with the isobar and is represented by a straight inclined line. In the superheated steam region the isotherm is depicted by a curve whose convex side faces upward (Fig. 12-3*a*).

On the *p-v* diagram, in the wet steam region, the isothermal process is represented by a horizontal line. For saturated steam this line coincides

with the isobar. In the superheated steam region steam pressure decreases, and the process is depicted by a curve whose convex side faces the abscissa (Fig. 12-3*b*). On the *T-s* diagram the isothermal process is represented by a horizontal line (Fig. 12-3*c*).

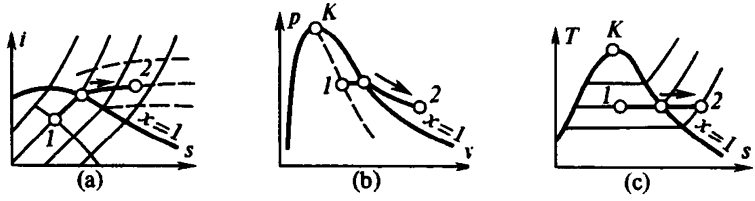


FIG. 12-3

In contrast to the internal energy of an ideal gas, the internal energy of steam changes due to the change of the potential-energy component and, therefore, at $T=\text{const}$

$$\Delta u=u_2-u_1=(i_2-p_2v_2)-(i_1-p_1v_1).$$

The quantity of heat added in the process is

$$q=T(s_2-s_1).$$

The external work is determined from the first law of thermodynamics

$$l=q-\Delta u.$$

Adiabatic Process. The adiabatic process is realized without addition or rejection of heat, and the entropy of the working medium undergoing a reversible process remains constant: $s=\text{const}$. That is why on the *i-s* and *T-s* diagrams adiabatic processes are represented by vertical straight lines (Fig. 12-4*a*, *b*). Upon adiabatic expansion, the pressure and temperature

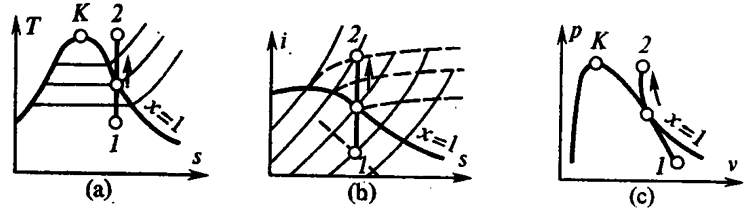


FIG. 12-4

of steam decrease; superheated steam turns into dry saturated, then—into wet steam. Under conditions of constant entropy it is possible to determine the final steam parameters, if the parameters of the initial state and one parameter of the final state are known.

On the *p-v* diagram a reversible adiabatic process is depicted by some curve, as shown in Fig. 12-4*c*.

The work done in an adiabatic process is determined from the equation

$$l=u_1-u_2=(i_1-p_1v_1)-(i_2-p_2v_2).$$

The change of internal energy

$$\Delta u=(i_2-p_2v_2)-(i_1-p_1v_1).$$

Typical Questions and Examples to Chapter Twelve

1. What methods are used to investigate thermodynamic processes associated with water vapour, or steam?
2. What equations are used to calculate the amount of heat added in an isochoric process, the change of internal energy, the work output and the dryness fraction?
3. What equations are used to determine the change of internal energy, external work, the amount of added heat and the dryness fraction in an isobaric process?
4. How are the change of internal energy, amount of added heat and the external work in isothermal process determined?
5. What peculiarity is involved in calculating an isothermal process with steam as a working medium, compared with an ideal gas?
6. How are the added heat, the change of internal energy and the external work done in an adiabatic process determined?
7. How are the main steam processes represented on *p-v*, *T-s* and *i-s* diagrams?

Example 12-1. With the aid of tables determine the final pressure, the degree of dryness and the quantity of rejected heat, if in a closed vessel with volume 2 m³ dry saturated steam is cooled from the initial temperature $t_1=180$ °C to the final temperature $t_2=58$ °C.

At $t_1=180$ °C the initial steam pressure $p_1=10$ bar and at $t_2=58$ °C the final pressure $p_2=0.18$ bar. With a constant volume $v_1=v_2=v''=0.1945$ m³/kg, $i_1=2778$ kJ/kg.

At the end of the process the dryness fraction

$$x_2=\frac{v_x-v'}{v''-v'}=\frac{0.1945-0.00113}{8.38-0.00113}=0.023.$$

The quantity of heat rejected in the isochoric process

$$q_v=u_2-u_1=(i_2-p_2v)-(i_1-p_1v).$$

We determine:

$$i_2=i_2'+rx_2=242+2363\times0.023=296 \text{ kJ/kg};$$

$$u_2=i_2-p_2v=296-\frac{1.18\times10^5\times0.1945}{1000}=292.5 \text{ kJ/kg};$$

$$u_1=i_1-p_1v=2778-\frac{10\times10^5\times0.1945}{1000}=2583 \text{ kJ/kg}.$$

Substituting the quantities thus obtained into the formula for q_v, we find that

$$q_v = u_2 - u_1 = 295.5 - 2583 = -2290.5 \text{ kJ/kg.}$$

Since the process involves 2 m³ of steam of mass

$$m = \frac{1}{0.1945} \times 2 = 10.286 \text{ kg,}$$

then

$$Q = mq_v = 10.286 \times (-2290.5) = -23\,550 \text{ kJ.}$$

Example 12-2. 1 kg of steam at a pressure $p_1 = 20$ bar and of a dryness fraction $x_1 = 0.85$ is heated at a constant pressure to 300 °C. Making use of tables and of the *i-s* diagram, determine the amount of heat involved in the process, the work due to expansion and the change of internal energy. The initial enthalpy of the steam is

$$i_1 = i' + rx_1 = 908.6 + 1890.7 \times 0.85 = 2515.5 \text{ kJ/kg.}$$

From the *i-s* diagram we find that the final enthalpy of the steam $i_2 = 3050$ kJ/kg, and the amount of heat

$$q_p = i_2 - i_1 = 3050 - 2515.6 = 534.4 \text{ kJ/kg.}$$

The work done by the steam

$$l = p(v_2 - v_1) = 20 \times 10^5 (0.128 - 0.09) = 76 \text{ kJ/kg;}$$

the change of internal energy

$$\Delta u = q - l = 534.4 - 76 = 458.4 \text{ kJ/kg.}$$

Example 12-3. Determine the quantity of heat added to steam, the change of internal energy and the work of expansion done when steam at a temperature $t = 300$ °C expands isothermally from a pressure $p_1 = 10$ bar to $p_2 = 1$ bar.

The amount of added heat can be determined either from the *i-s* diagram or with the aid of tables

$$q = T(s_2 - s_1) = 573(8.26 - 7.02) = 704 \text{ kJ/kg.}$$

The change in the internal energy of steam is equal to

$$\Delta u = (i_2 - p_2 v_2) - (i_1 - p_1 v_1) = \left(3080 - \frac{1 \times 2.69 \times 10^5}{1000}\right) -$$

$$- \left(3050 - \frac{10 \times 0.263 \times 10^5}{1000}\right) = 23 \text{ kJ/kg.}$$

The internal energy of superheated steam is a function not only of temperature, but also of volume.

The work of expansion

$$l = q - \Delta u = 704 - 23 = 681 \text{ kJ/kg.}$$

Example 12-4. At a pressure of 80 bar and temperature $t=500$ °C superheated steam expands adiabatically to $p_2=0.1$ bar. Determine on the *i-s* diagram the final state of the steam, the change in internal energy and the external work.

We find on the *i-s* diagram that at the end of expansion the steam shall be wet with a dryness fraction $x=0.81$. The initial parameters

$i_1=3405$ kJ/kg; $v_1=0.046$ m³/kg.

The final parameters

$i_2=2130$ kJ/kg; $v_2=12.7$ m³/kg.

The change in internal energy amounts to

$$\Delta u=i_2-i_1-(p_2v_2-p_1v_1)=2130-3405-\left(\frac{0.1\times10^5\times12.7}{1000}-\frac{80\times10^5\times0.046}{1000}\right)=$$

$$=-1034 \text{ kJ/kg}.$$

The work of expansion is equal to

$l=u_1-u_2=1034$ kJ/kg.

CHAPTER THIRTEEN

FLUID FLOW PROCESSES

13-1. Application of the First Law of Thermodynamics to Gases in Flow

A great number of machines are in operation, in which work is performed at the expense of the external kinetic energy of the working medium: steam turbines, gas turbines, jet engines, rockets and others.

In processes involving a change of state of a gas moving with a finite velocity heat is spent not only to change the internal energy and to perform work on the surrounding medium (against external forces), but also to increase the external kinetic energy of the gas as it moves along the conduit. That is why the equation of the first law of thermodynamics acquires the following appearance:

$$dq = du + dl' + \frac{dw^2}{2}, \tag{13-1}$$

where dq = heat transferred to the working medium from external heat sources;

du = change in the internal energy of the gas;

dl' = work done against the external forces, referred to as *displacement work* (it is not equal to the work due to expansion of the gas, dl);

$\frac{dw^2}{2}$ = change in the external kinetic energy of the working medium *(the availability)*.

In deriving Eq. (13-1), no allowance was made for the effect of gravitational forces and also it was assumed that the gas did not perform the so-called *mechanical* (or *shaft*) *work* (see Sec. 13-2).

The kinetic energy of a working medium may change both in tubes of a uniform cross-sectional area and in special channels of variable cross-sectional area, called nozzles and diffusers.

If a gas moving along a duct expands, resulting in a decrease in pressure and an increase in speed, such a duct is called a *nozzle.*

If the working medium is compressed in the duct, resulting in an increase in pressure and decrease in speed, such a duct is referred to as a *diffuser.*

13-2. Displacement Work. Further Extension of the Equation of the First Law of Thermodynamics to Flow

Let us determine the magnitude of the work done against external forces or the displacement work dl'. In deriving the equation, the following conditions of flow are assumed. The flow is assumed to be continuous, i.e. it is assumed that the same mass of the working medium passes through any cross section of the duct per unit time

$$m=f_1w_1/v_1=f_2w_2/v_2=fw/v=\text{const}, \tag{a}$$

where $f_1, f_2, \ldots, f$ = cross-sectional areas of the duct;
$w_1, w_2, \ldots, w$ = speeds of the working medium;
$v_1, v_2, \ldots, v$ = specific volumes.

The gas flows along the duct without addition or rejection of heat, i.e. the flow is adiabatic.

In each cross section of the duct the speed w, pressure p, temperature T and other properties of the working medium are constant over the cross section of the duct, i.e. the properties are the same at all points lying on the plane that is square with the axis of the duct (averaged values).

The motion, or flow, is considered to be *steady-state*. The quantities v, w, p, T can vary along the length of the duct, but in each section, to which they pertain, they are independent of time. All quantities are only functions of coordinates.

Let us assume that a gas flows along a variable cross-sectional area duct (Fig. 13-1). Let us consider an elementary mass of gas between the sections

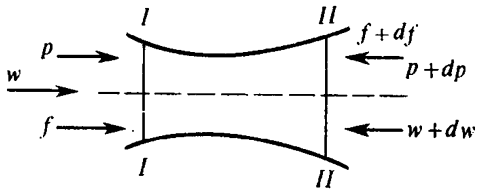


FIG. 13-1

I-I and *II-II*. Force pf acts in section *I-I*, and force $(p+dp)(f+df)$, oppositely directed to force pf, acts in section *II-II*. The two forces, acting in sections *I-I* and *II-II*, perform work; the algebraic sum of these works shall be equal to the work expended to displace the elementary mass of gas. The elementary displacement work done on an infinitely small path between the sections *I-I* and *II-II* per second is found from the equation

$$dl'_\tau=(p+dp)(f+df)(w+dw)-pfw.$$

Removing the brackets and dropping the infinitely small quantities of the second and higher orders, we obtain

$$dl'_\tau=dp(fw)+fw\,dp. \tag{b}$$

It follows from Eq. (a) that

$$mv=fw,$$

where m is the mass of gas flowing through any section of the duct in one second.

Replacing in Eq. (b) the quantity fw with mv, we get

$$dl'_{\tau}=m(p\,dv+v\,dp),$$

or

$$dl'_{\tau}=m\,d(pv).$$

Thus, the elementary displacement work per unit mass is

$$dl'_{\tau}=d(pv). \tag{13-2}$$

For a gas in flow the differential equation of the first law of thermodynamics takes the appearance

$$dq=du+d(pv)+dw^2/2,$$

or

$$dq=d(u+pv)+dw^2/2.$$

The quantity in brackets, $(u+pv)$, is the enthalpy, hence,

$$dq=di+dw^2/2 \tag{13-3}$$

or

$$q=i_2-i_1+\frac{w_2^2-w_1^2}{2}.$$

Equation (13-3) indicates that the heat added in a fluid flow (gas or liquid) is expended to change the internal energy, perform displacement work and to change the external kinetic energy of the working medium, or, with a fluid in flow, the added heat is spent to change its enthalpy and the external kinetic energy.

When 1 kg of a moving gas performs useful work l_{mech} on an external object and its potential energy of change in elevation $(h-h_1)$ changes, the law of conservation of energy leads to the following equation:

$$\left(i_1+\frac{w_1^2}{2}\right)-\left(i_2-\frac{w_2^2}{2}\right)=q-l_{mech}-g(h-h_1), \tag{13-4}$$

or in the differential form

$$di+\frac{dw^2}{2}=dq+dl_{mech}-g\,dh.$$

The derived equation is true both for reversible and irreversible (accompanied by friction) processes. In fact, in the presence of friction, there should be spent shear work l_{fr}, due to fluid friction, that fully converts into heat q_{fr}.

As the shear work l_{fr} is equal to the friction heat q_{fr} the two quantities, having opposite signs, cancel each other and drop out of Eq. (13-4).

When there is no heat exchange between the flowing working medium and the surroundings (adiabatic flow) with $h_2=h_1$ and $l_{mech}=0$, which is most commonly encountered, Eq. (13-4) takes the form

$$di+\frac{dw^2}{2}=0$$

or

$$i_1-i_2=\frac{w_2^2-w_1^2}{2}. \tag{13-5}$$

The change in the external kinetic energy of the working medium is due to the change in its enthalpy. When the initial velocity of the working medium is equal to zero, then flow velocity is determined by formula

$$w=\sqrt{2(i_1-i_2)}.$$

If enthalpy is measured in units of kJ/kg, the above equation becomes

$$w=44.72\sqrt{i_1-i_2}. \tag{13-6}$$

The enthalpies i_1 and i_2 are determined from the *i-s* diagram or from the tables compiled for the given substance.

13-3. Availability in Gas Flow Processes

The quantity $\frac{dw^2}{2}$, equal to the infinitely small increment of the internal kinetic energy of the working medium, is called the *elementary available work* or *availability*. This energy can be used to produce external useful work on the surroundings.

Comparing Eqs. (5-13) and (13-3), it is clear that for reversible gas flow

$$\frac{dw^2}{2}=-v\,dp \quad \text{or} \quad w\,dw=-v\,dp. \tag{13-7}$$

Equality (13-7) shows that when a working body flows along a duct, or conduit, the signs of dw and dp are opposite. If $dp>0$, then the gas is being compressed and its velocity decreases: $dw<0$.

If $dp<0$ the gas expands and its velocity increases: $dw>0$.

With a gas in flow the availability can be represented graphically on a *p-v* diagram. Shown graphically in Fig. 13-2 is a reversible process of gas expansion, line *1-2*.

The infinitely small availability $v\,dp$, is measured by the infinitely small elementary area *ab dc*. It is clear that all the work available in the process *1-2* is equal to

$$l_{av}=\int_{p_1}^{p_2}-v\,dp=\int_{p_2}^{p_1}v\,dp. \tag{13-8}$$

As it follows from Eqs. (5-13) and (13-3) the increase in the kinetic energy of the gas flow (available work) is equal to the difference between the work of gas expansion, $\int_{v_1}^{v_2} p\,dv$, and the displacement work $(p_2v_2-p_1v_1)$. The l_{av} (availability) is represented by the area *1234* bounded between the line of the process of gas expansion, abscissas of the extreme points and the ordinate axis p.

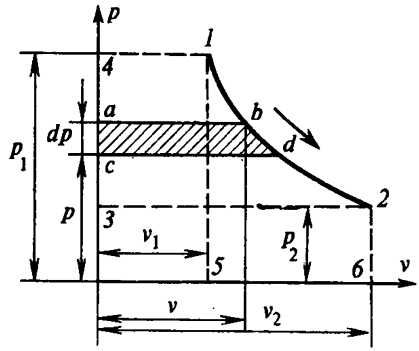


FIG. 13-2

If the curve *1-2* is a polytropics, then the availability is determined from equation

$$l_{av}=\int_{p_2}^{p_1} v\,dp=\int_{p_2}^{p_1} v_1(p_1/p_2)^{1/n}\,dp=[n/(n-1)](p_1v_1-p_2v_2). \qquad (13\text{-}9)$$

Upon adiabatic expansion of an ideal gas

$$l_{av}=\int_{p_2}^{p_1} v_1(p_1/p_2)^{1/k}\,dp=[k/(k-1)](p_1v_1-p_2v_2). \qquad (13\text{-}10)$$

Comparing the available work of a flow process (area *1234*) with the work due to gas expansion (area *1265*), we see that the available work is n times greater than the work due to gas expansion

$$l_{av}=nl.$$

It follows from Eq. (13-3) that

$$dl_{av}=dw^2/2=dq-di$$

or

$$l_{av}=q+i_1-i_2.$$

With a gas in flow the available work can be ensured at the expense of external heat and the decrease of the enthalpy of the gas. This equation is valid both for reversible and irreversible frictional gas flow processes.

With adiabatic flow it follows from Eq. (13-5) that

$$dl_{av}=dw^2/2=-di,$$

whence

$$l_{av}=(w_2^2-w_1^2)/2=i_1-i_2. \tag{13-11}$$

With irreversible gas flow and the same pressure drop the available work shall be smaller, since in the final state the enthalpy shall be larger at the expense of the added frictional heat. In practice, calculations are usually carried out for an ideal (reversible) flow process, and the irreversibility of the actual process is accounted for by an empirical coefficient that is always less than unity.

13-4. Adiabatic Gas Flow Processes

Experimental and theoretical studies show that even at a small difference between the pressures of a gas and of the surrounding medium the working medium may flow in a duct with a fairly high velocity. Since the length of the duct is not great and if the time spent by the gas in it is small, the heat exchange between the walls of the duct and the gas is so insignificant that it can be ignored and the process of flow may be assumed to be adiabatic.

In an adiabatic process the velocity of gas flow can be determined from the main equation for the available work

$$dl_{av}=dw^2/2,$$

or

$$l_{av}=\int_1^2 dw^2/2=(w_2^2-w_1^2)/2,$$

whence

$$w_2=\sqrt{2l_{av}+w_1^2},$$

where w_1 = initial gas velocity;
w_2 = final gas velocity at the outlet from the duct.

In most cases the inlet velocity of the gas is rather small as compared with its outlet velocity, and in practical calculations it is usually ignored.

Then, the velocity of gas flow is determined from equation

$$w=\sqrt{2l_{av}}=\sqrt{2(i_1-i_2)}. \tag{13-12}$$

13-5. Fluid Flow Processes

The velocity of fluid flow is determined from Eq. (13-12).

The available work of an incompressible liquid (at $v=\text{const}$)

$$l_{av}=\frac{w^2}{2}=-\int_{p_1}^{p_2} v\,dp=v\int_{p_2}^{p_1} dp=v(p_1-p_2)=\frac{p_1-p_2}{\varrho}$$

and

$$w=\sqrt{2v(p_1-p_2)}=\sqrt{2(p_1-p_2)/\varrho}, \qquad (13\text{-}13)$$

where p_1 and p_2 = the initial and final pressures of liquid;
ϱ = density of liquid.

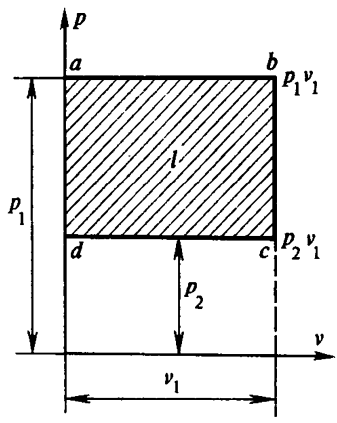


FIG. 13-3

The available work of fluid flow is presented graphically by the area of the rectangle *abcd* (Fig. 13-3).

13-6. The Velocity and Rate of Flow of an Ideal Gas Through a Converging Nozzle

For an ideal gas in adiabatic flow the available work is determined from Eq. (13-10), and the velocity of adiabatic flow of the ideal gas through a nozzle is found from Eq. (13-12)

$$w=\sqrt{2l_{av}}=\sqrt{2\left[\frac{k}{(k-1)}\right](p_1v_1-p_2v_2)},$$

or

$$w=\sqrt{2\left[\frac{k}{(k-1)}\right]p_1v_1[1-(p_2/p_1)^{(k-1)/k}]}. \qquad (13\text{-}14)$$

The velocity of gas flow depends on the state of the gas at the inlet to the nozzle and on pressure p_2 at the outlet from the nozzle.

The mass rate of gas flow, measured in kilograms per second, is determined from equation

$$m=fw/v_2, \qquad (13\text{-}15)$$

where f = exit area of the duct;
w = velocity of flow;
v_2 = specific volume of gas at the exit section of the duct.

With an ideal gas in adiabatic flow

$$v_2=v_1(p_1/p_2)^{1/k}.$$

Then, the rate of mass flow of the ideal gas is

$$m=\frac{f\sqrt{2[k/(k-1)](p_1v_1)[1-(p_2/p_1)^{k-1/k}]}}{v_1(p_1/p_2)^{1/k}}$$

or

$$m=f\sqrt{2[k/(k-1)](p_1/v_1)[(p_2/p_1)^{2/k}-(p_2/p_1)^{(k+1)/k}]}. \quad (13\text{-}16)$$

The mass flow rate of an ideal gas depends on the area of the outlet section of the duct, initial state of the gas and the degree of expansion.

For an ideal gas in flow the available work is represented graphically by the area *abcd* in Fig. 13-4.

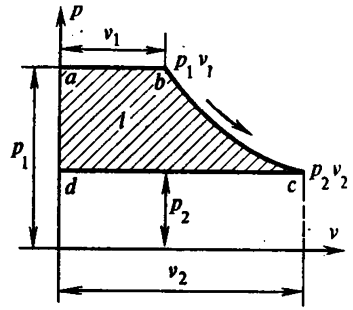


FIG. 13-4

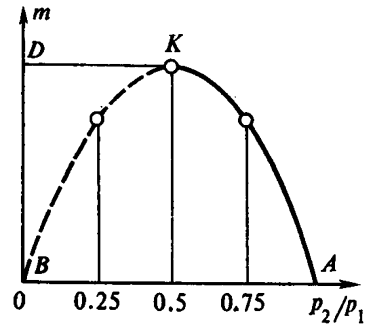


FIG. 13-5

13-7. Analysis of the Equation for the Mass Flow Rate of an Ideal Gas and Critical Pressure

The mass flow rate of an ideal gas, determined by Eq. (13-16), depends on the pressure ratio p_2/p_1.

It follows from this equation that when $p_2=p_1$ the rate of flow m becomes zero. With a decrease in the surrounding medium pressure p_2 the rate of flow increases. At a certain pressure ratio $p_2/p_1=\beta_{cr}$ the rate of gas flow becomes maximum. With a further decrease of the ratio p_2/p_1 the quantity m diminishes and at $p_2/p_1=0$ it will again be equal to zero.

If in a system of coordinates p_2/p_1 and m (Fig. 13-5) different values of the ratio p_2/p_1 are plotted on the abscissa, and corresponding actual and calculated rates of gas flow m—on the axis of ordinates, we obtain a diagram of the rate of gas flow. The curve AK shows that with a decrease of the ratio p_2/p_1 the rate of gas flow increases. At a certain value of the ratio $p_2/p_1=\beta_{cr}$ the rate of flow reaches a maximum. With a further decrease of the ratio p_2/p_1 the actual rate of mass flow remains constant and is represented by curve KD, and the rate of flow m, calculated by Eq. (13-16), drops again to zero (curve KB).

Consequently, for $\beta_{cr}<p_2/p_1<1$ experimental results fully coincide with the results obtained in Eq. (13-16), and for $0<p_2/p_1<\beta_{cr}$ the experimental and analytical results fall apart.

To explain the discrepancy between analytical and experimental data the scientists de Saint-Venant and G. Wentzel suggested the following hypoth-

esis: for values $\beta_{cr}<p_2/p_1<1$ the pressure at the exit section of a converging nozzle is equal to the back pressure, therefore theoretical data coincide with experimental results. For $0<p_2/p_1<\beta_{cr}$ the pressure at the exit section of the convergent duct is no more equal to the medium, or back, pressure and, even though back pressure is reduced to a complete vacuum, the pressure at the exit section of the conduit remains constant.

It was indicated above that at $p_2/p_1=\beta_{cr}$ the mass flow per second reaches its maximum value. The variable value in Eq. (13-16) is

$$\left(\frac{p_2}{p_1}\right)^{2/k}-\left(\frac{p_2}{p_1}\right)^{(k+1)/k}$$

therefore to find the maximum, we take the first derivative of this quantity, equate it to zero, and the value of p_2/p_1, that transforms the derivative into zero, is precisely β_{cr}.

We have

$$\frac{\partial}{\partial\beta}(\beta^{2/k}-\beta^{(k+1)/k})=\frac{2}{k}\beta^{(2/k)-1}-\frac{k+1}{k}\beta^{[(k+1)/k]-1}=0,$$

whence

$$\beta_{cr}=\frac{p_{cr}}{p_1}=\left(\frac{2}{k+1}\right)^{k/(k-1)}. \qquad (13\text{-}17)$$

The quantity β_{cr} only depends on the adiabatic index k, i.e. depends on the nature of the working medium.

For a monatomic gas $k=1.66$ and $\beta_{cr}=0.49$.
For a diatomic gas $k=1.4$ and $\beta_{cr}=0.528$.
For a triatomic gas $k=1.3$ and $\beta_{cr}=0.546$.

Equation (13-17) can be used to determine the pressure at the outlet section of a nozzle when the maximum rate of flow, or discharge, is reached or the so-called *critical pressure*

$$p_{cr}=\beta_{cr}p_1, \qquad (13\text{-}18)$$

Thus, the critical pressure is equal to the initial, or inlet, pressure multiplied by the coefficient β_{cr}.

With a given inlet pressure, the critical pressure shall be the minimum pressure that sets in at the outlet section of a nozzle.

13-8. Critical Velocity and the Maximum Discharge of an Ideal Gas

The velocity of a gas that sets in at the outlet section of a converging nozzle during a flow in the surrounding medium having a pressure, equal to or lower than the critical, is referred to as the *critical velocity*. It can be

determined from Eq. (13-14) replacing in the equation the ratio p_2/p_1 with the value of $\beta_{cr}=[2/(k+1)]^{k/(k-1)}$

$$w=\sqrt{2[k/(k-1)]p_1v_1[1-(p_2/p_1)^{(k-1)/k}]};$$

$$w_{cr}=\sqrt{2\left[\frac{k}{(k-1)}\right]p_1v_1\left(1-\frac{2}{k+1}\right)};$$

$$w_{cr}=\sqrt{2\left[\frac{k}{(k+1)}\right]p_1v_1}. \qquad (13\text{-}19)$$

For an ideal gas the critical velocity only depends on the initial properties and nature of the gas.

Critical velocity can be shown to be equal to the velocity of sound at p_{cr} and v_{cr}.

From the adiabatic process it follows that

$$v_1=v_{cr}\left(\frac{p_{cr}}{p_1}\right)^{1/k}$$

From Eq. (13-17) we find

$$p_1=p_{cr}\left(\frac{k+1}{2}\right)^{k/(k-1)}$$

or

$$v_1=v_{cr}\left(\frac{p_{cr}}{p_{cr}\left(\frac{k+1}{2}\right)^{k/(k-1)}}\right)^{1/k}=\left(\frac{2}{k+1}\right)^{1/(k-1)}v_{cr}$$

and

$$v_1p_1=p_{cr}\left(\frac{k+1}{2}\right)^{k/k-1}\cdot v_{cr}\left(\frac{2}{k+1}\right)^{1/(k-1)},$$

whence

$$p_1v_1=v_{cr}p_{cr}\left(\frac{k+1}{2}\right).$$

Substituting the quantity p_1v_1 into formula (13-19), we obtain the value of critical velocity w_{cr}:

$$w_{cr}=\sqrt{\left(\frac{2k}{k+1}\right)v_{cr}p_{cr}\left(\frac{k+1}{2}\right)},$$

and, upon transformation, we have

$$w_{cr}=\sqrt{kp_{cr}v_{cr}}. \qquad (13\text{-}20)$$

Of great importance in the thermodynamic theory of gas flow is the velocity of sound. The speed of propagation of sound is determined from the Laplace equation

$$a=\sqrt{k(p/\varrho)}=\sqrt{kpv}$$

where p = pressure of the medium in which sound propagates; N/m^2;
ϱ = density of the medium, kg/m^3.

For an ideal gas

$$a=\sqrt{kRT}.$$

The speed of propagation of elastic deformation, i.e. the velocity of sound, depends on the state and nature of the gas and is a direct function of temperature. This permits the conclusion that for each section of a duct there should exist a local velocity of sound, determined by the magnitude of pressure p and volume v at the given section.

The quantity $a=\sqrt{kv_{cr}p_{cr}}$ determines the velocity of sound in a gas in flow at critical parameters at the outlet section of a divergent nozzle, or the critical velocity of gas flow through a nozzle is equal to the local velocity of sound (at the given section), i.e. $w_{cr}=a$.

The foregoing makes it possible to explain why in a convergent nozzle a gas cannot expand to a pressure below the critical, and its velocity cannot exceed the critical. In fact, as is known from physics, a pressure pulse propagates in a material medium with the velocity of sound and therefore, when flow velocity is lower than the velocity of sound (critical velocity), the decrease in back pressure is transmitted along the gas flow inside the duct and causes a redistribution of pressure in it. As a result the pressure at the outlet section becomes equal to the back pressure. But if the flow velocity reaches the velocity of sound (critical velocity), then the gas flow velocity in the outlet section and the speed of pressure propagation shall be equal and no decrease in back pressure shall affect the distribution of pressure along the duct. The pressure shall be constant and, consequently, the pressure at the outlet section of the duct shall also be constant irrespective of the magnitude of the back pressure.

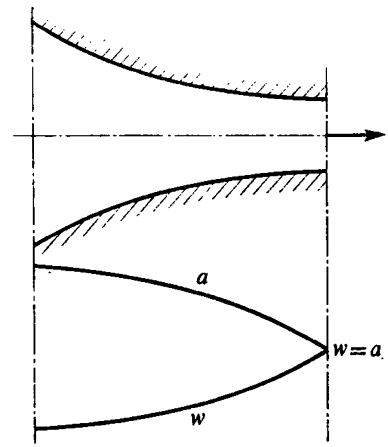


FIG. 13-6

It follows from the foregoing that the velocity of flow at the exit section of a divergent nozzle cannot be greater than the velocity of sound in a gas (Fig. 13-6).

With a critical pressure at the outlet section of the duct a maximum rate of gas flow, or discharge, sets in, that can be determined from Eq. (13-16), by replacing the ratio p_2/p_1 with its value from Eq. (13-17).

Upon corresponding transformations we obtain

$$m_{max}=f_{min}\sqrt{2\left(\frac{k}{k+1}\right)\frac{p_1}{v_1}\left(\frac{2}{k+1}\right)^{2/(k-1)}}. \qquad (13\text{-}21)$$

The maximum rate of gas flow is fully determined by the initial state of the gas, the area of the exit section, f_{min}, and by the nature of the gas, i.e. by the adiabatic index k.

13-9. Main Conditions for Flow of Ideal Gases Through Variable-Section Ducts

Under conditions of continuity of flow and steady-state rate the same mass of the working medium flows in unit time through any cross section of a duct, then

$$fw=mv. \qquad (a)$$

Differentiating Eq. (a) at $w=$const, we obtain

$$f\,dw+w\,df=m\,dv. \qquad (b)$$

Dividing Eq. (b) by Eq. (a), we find

$$\frac{df}{f}=\frac{dv}{v}-\frac{dw}{w}. \qquad (13\text{-}22)$$

Equation (13-22) determines the conditions for continuity of flow and shows that the shape of the duct depends on the change in the volume of the gas and its velocity.

Let us investigate this equation for the case of adiabatic expansion of an ideal gas. For this purpose substitute into the equation the value of dv/v from the equation of an adiabat, and dw/w—from the equation of available work.

Upon differentiation of the equation of an adiabat,

$$pv^k=\text{const},$$

we obtain

$$\frac{dv}{v}=-\frac{1}{k}\cdot\frac{dp}{p}.$$

From Eq. (13-7) we find that

$$\frac{dw}{w}=-\frac{v\,dp}{w^2}.$$

Substituting the quantities $\frac{dv}{v}$ and $\frac{dw}{w}$ into Eq. (13-22), we obtain

$$\frac{df}{f}=-\frac{1}{k}\frac{dp}{p}+\frac{v\,dp}{w^2}=\frac{dp}{\frac{v}{w^2}-\frac{1}{kp}}$$

and

$$\frac{df}{f}=\frac{dp(kvp-w^2)}{w^2kp}, \qquad (13\text{-}23)$$

but the quantity kvp is the squared velocity of sound, a^2, hence

$$\frac{df}{f}=\frac{dp(a^2-w^2)}{w^2kp}. \tag{13-24}$$

Let us analyze the derived Eq. (13-24), applying it to two ducts: a nozzle and a diffuser.

Let a gas flow through a nozzle ($dp<0$). It follows from Eq. (13-24) that the sign of quantity df is then opposite to the sign of (a^2-w^2). If $(a^2-w^2)>0$ and $w<a$, then $df<0$; the section of the nozzle must diminish in the direction of gas flow and the velocity of the gas shall be smaller than the local velocity of sound. If $(a^2-w^2)<0$ and $w>a$, then the section of the nozzle must increase in the direction of gas flow and the velocity of gas shall be smaller than the local sound velocity. In the narrowest cross section of the nozzle, referred to as the throat, the velocity of the gas shall be equal to the velocity of sound which is the maximum velocity of a gas in adiabatic flow through a convergent nozzle. For the flow of a gas through a nozzle to become supersonic, i.e. to ensure supersonic velocites of gas flow, the nozzle must be built up of a convergent inlet part and a divergent outlet part.

Let a gas flow through a diffuser ($dp>0$). If in Eq. (13-24) $(a^2-w^2)>0$ and $w<a$, then $df>0$; if gas velocity at the inlet to the duct is smaller than the velocity of sound, the diffuser must diverge in the direction of gas flow. If $(a^2-w^2)<0$ and $w>a$, then $df<0$; if the velocity of the gas at the inlet to the duct is greater than the velocity of sound, the diffuser must converge in the direction of gas flow.

Thus, depending on gas velocity at the inlet, a duct may serve both as a nozzle and as a diffuser.

13-10. Flow of an Ideal Gas Through a Convergent Nozzle

First case. The back pressure exceeds the critical pressure, or when $\beta_{cr}<\frac{p_2}{p_1}<1$. In these conditions the entire pressure drop from p_1 to p_2 is consumed (Fig. 13-7) and complete expansion of the gas takes place. Gas velocity at the outlet section of the nozzle is less than the velocity of sound (Fig. 13-8). Gas pressure at the outlet section of the nozzle is equal to back pressure.

The velocity at the outlet section and the rate of gas flow with a given outlet area are determined by formulae (13-14) and (13-16).

The exit area of the nozzle, f, can be determined from formula (13-16), provided the rate of flow is given

$$f=\frac{m}{2\left(\frac{k}{k-1}\right)\frac{p_1}{v_1}\left(\frac{p_2}{p_1}\right)^{2/k}\left(\frac{p_2}{p_1}\right)^{k+1/k}}; \tag{13-25}$$

the available work, l_{av}, is presented by area *1234* in Fig. 13-7.

Second case. The back pressure is lower than the critical, or $0<p_2/p_1<\beta_{cr}$. In these conditions not the entire pressure drop, from p_1 to p_2, is used but only a part of it, from p_1 to p_{cr} (Fig. 13-9); incomplete expansion of the gas takes place, and the velocity at the outlet section of the convergent nozzle

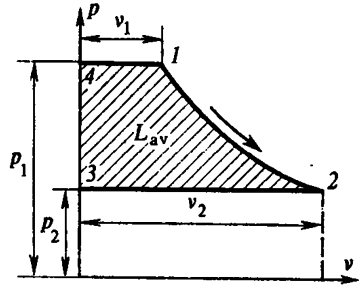


FIG. 13-7

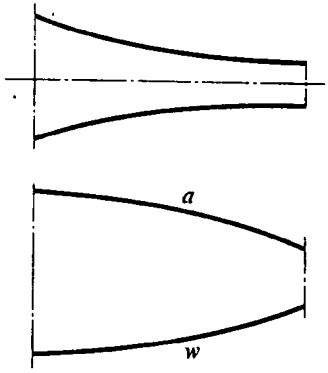


FIG. 13-8

is equal to the critical or local velocity of sound (Fig. 13-6). The pressure at the nozzle outlet section is equal to critical pressure

$$p_{cr}=p_1\beta_{cr}.$$

The critical velocity of flow through the nozzle and the maximum rate of flow of an ideal gas are determined by formulae (13-19) and (13-21).

With a given rate of flow the outlet area of a nozzle (which is also the minimum cross-sectional area) is determined by formula (13-21)

$$f_{\min}=\frac{m_{\max}}{\sqrt{2\frac{k}{k+1}\frac{p_1}{v_1}\left(\frac{2}{k+1}\right)^{2/(k-1)}}}.$$

The available work, l_{av}, is presented by area *1234* in Fig. 13-9.

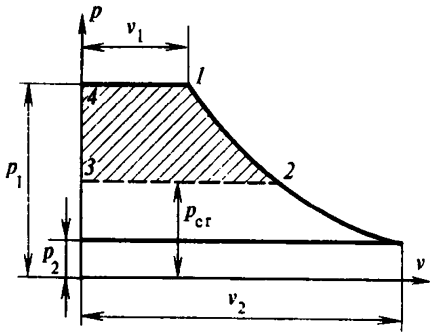


FIG. 13-9

13-11. Flow of an Ideal Gas Through a Combined Laval Nozzle

The combined Laval nozzle is designed to utilize large pressure drops and to obtain flow velocities in excess of the critical velocity or the velocity of sound.

The Laval nozzle comprises a convergent part and a divergent conical part as illustrated in Fig. 13-10. It has been shown experimentally that the divergence angle of the nozzle should be $\Omega = 8$ to $12°$. With larger angles of divergence separation of the flow from the walls of the duct is observed.

When a gas flows through a combined nozzle into a surrounding medium at a pressure lower than critical, a critical pressure p_{cr} and critical velocity w_{cr} set in at the narrowest section of the combined nozzle, referred to as the throat.

In the divergent part of the combined nozzle a further increase in gas velocity takes place and the pressure drops to that of the surrounding medium, referred to as back pressure.

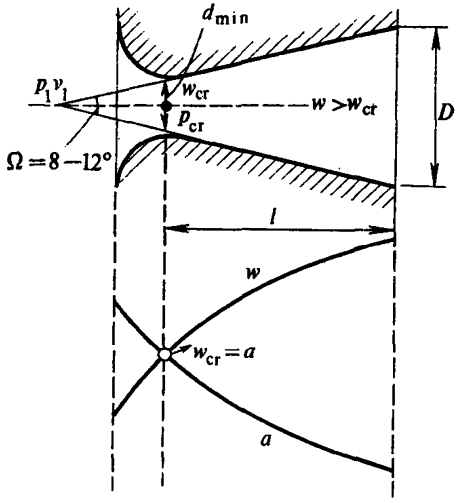


FIG. 13-10

The velocity of flow at the outlet section and the rate of flow of an ideal gas (at a given f) are determined by formulae (13-14) and (13-16).

With a given rate of flow the minimum cross-sectional area of the nozzle, or the throat area, f_{min}, can be calculated by formula (13-21) and the outlet area of the nozzle, f,—by formula (13-16).

The length of the convergent part of the combined nozzle is usually assumed equal to the diameter of the critical outlet section of the nozzle. The length of the divergent part of the combined nozzle, l (Fig. 13-10), can be determined from equation

$$l = \frac{D-d}{2} \tan \frac{\Omega}{2},$$

where Ω = angle of divergence of the nozzle;
D = diameter of the exit section;
d = diameter of the nozzle throat.

13-12. Flow of Gases With Friction

The formulae derived above for the velocity and rate of flow through ducts are valid only for cases of reversible flow, since the formulae ignore the friction of the working medium against the walls of the duct, skin friction, and the internal friction between jets of the flow due to difference between flow velocities over the cross section of the duct.

With account taken of the friction forces for the same pressure drop Δp across any duct the velocity of gas flow shall be lower than the velocity in a reversible flow process (the theoretical velocity).

The ratio of the real gas velocity w_r to the theoretical velocity w is called the *velocity coefficient*

$$\varphi_v = \frac{w_r}{w} \quad \text{and} \quad w_r = \varphi_v w. \tag{13-26}$$

According to experimental data, for properly machined ducts the velocity coefficient φ_v varies from 0.96 to 0.98. Values of the velocity coefficients are given in special courses on steam turbines and general heat engineering.

The presence of frictional forces makes the adiabatic process irreversible. The kinetic energy of flow, expended to overcome the frictional forces, converts into heat that is transferred to the gas; this heat raises the enthalpy of the working medium at the exit from the duct.

The loss of kinetic energy is equal to

$$\frac{w^2 - w_r^2}{2} = \frac{w^2 - \varphi_v^2 w^2}{2} = (1 - \varphi_v^2)\frac{w^2}{2} = \psi \frac{w^2}{2},$$

where the quantity $\psi = 1 - \varphi_v^2$ is called the *energy loss coefficient.*

The ratio of the real kinetic energy of the working medium, $\frac{w_r^2}{2}$, to the theoretical energy $\frac{w^2}{2}$ is referred to as the *efficiency of a duct* and is denoted by η_d

$$\eta_d = \frac{\frac{w_r^2}{2}}{\frac{w^2}{2}} = \frac{w_r^2}{w^2} = \varphi_v^2 \frac{w^2}{w^2} = \varphi_v^2. \tag{13-27}$$

The efficiency of a duct is equal to the squared gas velocity coefficient. With no account taken of the initial velocity, frictional heat is equal to

$$q_{fr} = \psi \left(\frac{w}{2}\right)^2 = \psi(i_1 - i_2),$$

where i_1 and i_2 are the enthalpies of the working medium in the beginning and at the end of a reversible (isentropic) process of expansion.

Equations (13-26) and (13-27) are valid both for ideal, or perfect, and real gases.

13-13. Flow of Water Vapour (Steam)

The main assumptions and formulae governing the flow of gases, Eqs. (13-14) to (13-16), derived in the preceding sections, pertain to ideal gases.

When dealing with steam, all formulae and regularities governing the flow of gases through ducts and nozzles can only be applied for approximate calculations, assuming that for superheated steam $k=1.3$ and for dry saturated steam—$k=1.135$.

Whenever use is made of the equations in which k is present, its value should be determined in each individual application by formulae (7-27) based on the properties of the real body in the initial and final states of process.

It is most expedient to calculate the velocity rate of flow of a working medium with the aid of the *i-s* diagram plotted for the given substance, using Eq. (13-6) derived from the equation of the first law of thermodynamics for flow processes and valid for any real substance.

If the velocity of flow at the outlet section is less than critical, it is calculated by the formula

$$w=44.72\sqrt{i_1-i_2},$$

where i_1 and i_2 are determined from steam tables or the *i-s* diagram by the initial parameters, final pressure and from the condition of the adiabatic process in which $s_1=s_2$.

In critical conditions of flow, the velocity of steam flow is calculated by formula

$$w_{cr}=44.72\sqrt{i_1-i_{cr}},$$

with i_1 kJ/kg being taken from steam tables or the *i-s* diagram for steam by the initial parameters.

The magnitude of the enthalpy i_{cr} cannot be determined directly since the magnitude of the critical pressure is usually not known. Therefore, in the critical section of a duct or nozzle, it is advisable to determine the parameters of steam with some error, making use of the relationships that are only valid for ideal gases and applying the trial and error method. For this purpose we first assume that $k=1.3$ and from the relationship

$$\frac{p_{cr}}{p_1}=\left(\frac{2}{k+1}\right)^{k/(k-1)}$$

we find p_{cr}, then from steam tables, allowing for $s_1=s_{cr}$, and by the known values of p_{cr} and s_{cr} we determine the specific volume at the critical section. Then from the relation for the adiabatic process

$$k=\frac{\log p_1/p_{cr}}{\log v_{cr}/v_1}$$

we find a new value of the exponent k and use it to calculate p_{cr} again.

This operation is repeated till the value of p_{cr}, used to determine k, coincides with its value calculated by the formula for the ratio p_{cr}/p_1.

It should be borne in mind that this calculation method is an approximate one, but in practical calculations it usually yields sufficiently good results.

The velocity of steam flow through a combined nozzle is calculated by formula (a)

$$w=44.72\sqrt{i_1-i_2},$$

where i_1 = enthalpy of steam at inlet to the nozzle, kJ/kg;
i_2 = enthalpy of steam at the parameters of the surrounding medium into which the steam flows, kJ/kg.

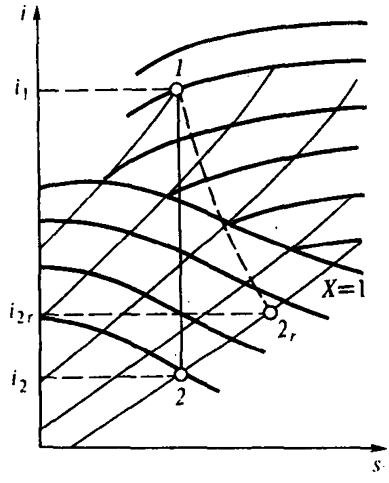


FIG. 13-11

The rate of mass flow (discharge) is determined from the continuity equation

$$m=\frac{fw}{v_2};$$

for critical conditions of flow

$$m_{\max}=f_{\min}\frac{w_{cr}}{v_{cr}}.$$

For irreversible flow processes

$$w_r=44.72\sqrt{i_1-i_{2r}}.$$

In Fig. 13-11 a reversible process is represented by line *1-2*, and an irreversible process—by the dotted curve *1-2r*. It is clear from the graphical illustration that in an irreversible process the enthalpy at the end of expansion shall be greater than in a reversible process, at the expense of frictional heat, as was already mentioned in Sec. 13-12.

Typical Questions and Examples to Chapter Thirteen

1. Write down the equation of the first law of thermodynamics for a flow process.
2. Explain the meaning of the quantities present in the equation for a flow process.
3. What ducts are referred to as nozzles and diffusers?
4. What state is said to be steady or stationary?
5. Write down the equation of continuity for a flow process.
6. Derive the equation for displacement work.
7. Equation of the first law of thermodynamics for a flow process with the use of enthalpy.

8. What causes a change in the internal kinetic energy of a working medium undergoing an adiabatic flow process?
9. What quantity is called the available work or availability?
10. Graphical representation of available work on a p-v diagram.
11. Equation of available work for polytropic and adiabatic processes.
12. Equation of available work for adiabatic flow processes with the use of enthalpy.
13. Velocity of adiabatic liquid flow.
14. Velocity of adiabatic flow of an ideal gas.
15. Rate of flow of an ideal gas.
16. Analysis of the equation for the rate of gas flow.
17. The de Saint-Venat and G. Wentzel hypothesis.
18. Critical pressure ratio and its determination.
19. Equation for determining the critical velocity of flow.
20. How is the velocity of sound determined?
21. Relation between the velocity of sound and the critical flow velocity.
22. How is the maximum rate of flow of an ideal gas determined?
23. Main conditions for gas flow through variable-section ducts.
24. What should be the shape of a nozzle at various gas inlet velocities?
25. What should be the shape of a diffuser at various gas inlet velocities?
26. What cases are encountered when a gas flows through a convergent nozzle?
27. Give a description of the combined Laval nozzle.
28. How are the velocity and rate of gas flow at the outlet section of a Laval nozzle determined?
29. How are the minimum (throat) and outlet areas of a Laval nozzle determined?
30. How is the length of a Laval nozzle determined?
31. The flow of steam through ducts and nozzles.
32. Flow of steam through a convergent nozzle under different conditions.
33. Flow of gases and vapours with friction.

Example 13-1. 1 kg of oxygen is discharged from a vessel at a temperature of 400 K and constant pressure $p_1=80$ bar through a convergent nozzle into a medium at a back pressure $p_2=60$ bar. Determine the velocity of flow at the outlet section and the rate of oxygen flow, if the nozzle outlet area $f=30$ mm^2. Also find the velocity and rate of flow if back pressure $p_2=20$ bar. In solving the problem assume oxygen to be an ideal gas.

The critical pressure ratio $\beta_{cr}=0.528$.

The ratio of pressures

$$\frac{p_2}{p_1}=\frac{60}{80}=0.75>0.528.$$

The discharge of oxygen takes place utilizing the entire pressure drop through the nozzle.

The initial volume

$$v_1=\frac{RT_1}{p_1}=\frac{259.82\times400}{80\times10^5}=0.013 \text{ m}^3/\text{kg};$$

flow velocity

$$w=\sqrt{2\left[\frac{k}{(k-1)}\right]p_1v_1\left[1-\left(\frac{p_2}{p_1}\right)^{(k-1)/k}\right]}=$$

$$=\sqrt{2\frac{1.4}{1.4-1}80\times10^5\times0.013\left[1-\frac{60}{80}^{\frac{1.4-1}{1.4}}\right]}=237 \text{ m/s};$$

the rate of oxygen flow per second

$$m=f\sqrt{2\left[\frac{k}{(k-1)}\right]\frac{p_1}{v_1}\left[\left(\frac{p_2}{p_1}\right)^{2/k}-\left(\frac{p_2}{p_1}\right)\right]^{(k+1)/k}}=$$

$$=0.00003\sqrt{2\frac{1.4}{1.4-1}\frac{80\times10^5}{0.013}\left[\left(\frac{60}{80}\right)^{\frac{2}{1.4}}-\left(\frac{60}{80}\right)^{\frac{1.4+1}{1.4}}\right]}=0.341 \text{ kg/s}.$$

When oxygen flows into a medium at a back pressure $p_2=20$ bar: the pressure ratio

$$\frac{p_2}{p_1}=\frac{20}{80}=0.25<0.258,$$

hence, oxygen shall leave the nozzle with a critical velocity; the flow velocity at the outlet section of the nozzle will be

$$w_{cr}=\sqrt{2\left(\frac{k}{k+1}\right)RT_1}=\sqrt{2\left(\frac{1.4}{2.4}\right)259.82\times400}=348 \text{ m/s}.$$

The maximum rate of oxygen flow per second

$$m_{\max}=f_{\min}\sqrt{2\frac{k}{k+1}\frac{p_1}{v_1}\left(\frac{2}{k+1}\right)^{2/(k-1)}}=$$

$$=0.00003\sqrt{2\frac{1.4}{1.4+1}\frac{80\times10^5}{0.013}\left(\frac{2}{1.4+1}\right)^{\frac{2}{1.4-1}}}=0.507 \text{ kg/s}.$$

Example 13-2. Wet steam at initial parameters $p_1=22$ bar and a dryness fraction $x_1=0.97$ flows from a combined nozzle into a medium at a back pressure $p_2=1$ bar. Find the velocity and state of the steam at the end of the process. Also determine the main dimensions of the nozzle, assuming $m=3.22$ kg/s.

The initial properties of state of the steam: $i_1=2750$ kJ/kg; $v''=0.091$ m³/kg; $x_1=0.97$; $v_1=v''x_1=0.0884$ m³/kg.

At a back pressure $p_2=1$ bar the final conditions of steam are: $i_2=2245$ kJ/kg; $x_2=0.81$; $v_2=0.81\times1.696=1.373$ m³/kg.

Steam flow velocity at the outlet section

$$w=44.72\sqrt{i_1-i_2}=44.74\sqrt{2750-2245}=1010 \text{ m/s.}$$

The outlet area of the combined nozzle

$$f_2=\frac{mv_2}{w}=\frac{3.22\times1.373}{1010}=0.0044 \text{ m}^2=44 \text{ cm}^2.$$

The length of the convergent part of the combined nozzle is usually assumed equal to throat diameter

$$l_1=d=\sqrt{\frac{1000}{0.785}}=35.7 \text{ mm.}$$

The diameter of the outlet section of the convergent part

$$D=\sqrt{\frac{4400}{0.785}}=74.8 \text{ mm.}$$

Let us assume an angle of divergence of the nozzle $\varphi=10°$. Then the length of the divergent part of the nozzle is determined from equation

$$l_2=\frac{D-d}{2\tan\varphi/2}=\frac{74.8-35.7}{2\tan 10/2}=223 \text{ mm.}$$

The length of the entire combined nozzle

$$l=l_1+l_2=35.7+233=258.7 \text{ mm}$$

CHAPTER FOURTEEN

THROTTLING OF GASES AND VAPOURS. MIXING OF GASES

14-1. Throttling of a Gas

Throttling is the name given to irreversible processes in the course of which the pressure of a gas flowing through a convergent hole diminishes without performing external work.

Any resistance offered to flow in a pipeline (valves, gate valves orifice, cock, etc.) causes throttling of a gas and, hence, a drop in pressure. The magnitude of the drop in pressure depends on the nature of the working medium, its state, the extent of convergence of the gas conduit and the velocity of gas flow.

Throttling is usually accompanied by a loss in the efficiency of the working medium and is certainly harmful. But sometimes there is a need for throttling and it is created artificially, for instance, in adjusting steam engines, in refrigerating installations, in instruments used to measure the rate of gas flow, etc.

As a gas passes through an opening offering a certain resistance to flow, the kinetic energy and velocity of the gas increase in the narrow section, which is accompanied by a drop in temperature and pressure (Fig. 14-1).

The gas, flowing through the opening, spends a fraction of its kinetic energy to perform work against forces of friction, and this work converts into heat. As a result gas temperature changes and may both decrease and increase.

The velocity of the gas rises in the opening. Beyond the opening, when the gas flows through the entire cross section of the conduit, the velocity decreases again, and the pressure increases, failing however to rise to its initial magnitude; a certain change in velocity shall take place as a result of the increase of the specific volume of the gas due to a decrease in pressure.

As was already mentioned, throttling is an irreversible process in the course of which the entropy of the working medium increases and its efficiency diminishes.

14-2. Equation of Throttling Process

Let there be a restriction to flow in a section of a pipeline as shown in Fig. 14-1. Sections *I-I* and *II-II* and the pipeline are closed with weightless pistons that are able to move without friction. Pressure p_1 acts upon the piston *1* with an area F_1 and piston *2* with an area F_2 is acted upon by

pressure p_2, with $p_1 > p_2$. There is no heat exchange between the pipeline and the surrounding medium.

As 1 kg of gas flows through the hole piston *1* shifts to position *1'*, and piston *2*—into position *2'*, with piston *1* covering the distance s_1, and piston *2*—the distance s_2. To displace 1 kg of the gas it is necessary to expend work $p_1 s_1 F_1$ or $p_1 v_1$. A fraction of this work, $p_2 F_2 s_2$ or $p_2 v_2$, shall be spent to overcome force p_2, and the difference between the works $p_1 v_1 - p_2 v_2$ will cause a change in the energy of the working medium.

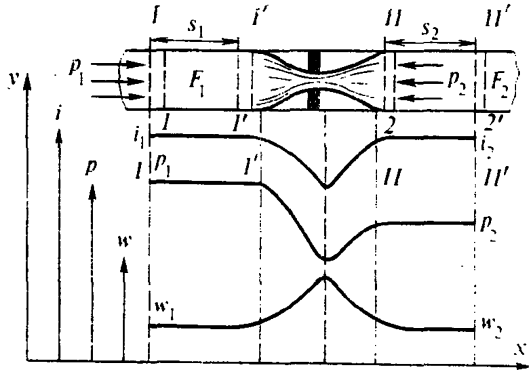


FIG. 14-1

If w_1 and w_2 are the initial and final gas velocities and u_1 and u_2 the corresponding internal enegies then we have

$$p_1 v_1 - p_2 v_2 = u_2 - u_1 + w_2^2/2 - w_1^2/2.$$

On condition that velocities w_1 and w_2 differ but little from each other, the change of the external kinetic energy can be ignored and considering the term $w_2^2/2 - w_1^2/2 = 0$,

$$(u_1 + p_1 v_1) - (u_2 + p_2 v_2) = 0$$

or

$$i_1 - i_2 = 0 \quad \text{and} \quad i_1 = i_2. \tag{14-1}$$

Equality (14-1) shows that enthalpy does not change as a result of throttling. This conclusion is not applicable to the intermediate states of a throttled gas. In the sections of the orifice enthalpy does not remain constant, i.e. the process of throttling cannot be identified with the isenthalpic process. Equality (14-1) is only valid for sections at a sufficient distance from the opening.

As mentioned above, the enthalpy of an ideal gas is a single-valued function of temperature. From this it follows that the temperature of an ideal gas undergoing throttling does not change ($T_1 = T_2$).

When a real gas undergoes throttling enthalpy remains the same in the initial and final states, the entropy and volume increase, gas pressure drops, and temperature may increase, diminish or remain unchanged in a special case.

14-3. Investigation of Throttling Process. Joule-Thomson Effect

In any real gas there are forces of molecular attraction and if the gas expands, a change in the distance between particles or a change of the internal potentional energy of the body always involves an expenditure of work which is associated with a change in temperature.

The ratio of the change of temperature of a real gas upon throttling without addition and rejection of heat and without the performance of external work, to the change of pressure in this process is called the *Joule-Thomson effect*. This effect was discovered by Joule and Thomson experimentally in 1852.

For an ideal gas the Joule-Thomson effect is zero, since the gas temperature does not change upon throttling. Consequently, the change of the temperature of a real gas undergoing throttling is due to the deviation of the properties of real gases from those of an ideal gas, which is due to the action of intramolecular forces.

The throttling of 1 kg of a working medium is accompanied by the expenditure or performance of external work (work of displacement), equal to $p_2v_1-p_1v_2$. In the expression for displacement work the product p_2v_2 characterizes the work spent by the working body to displace the surrounding medium, and the product p_1v_1—the work done by the surrounding medium on the working medium. Since in the course of throttling the final pressure p_2 is always smaller than the initial pressure p_1, and the specific volume v_2 is always larger than v_1, then the difference $p_2v_2-p_1v_1$ can generally be positive or negative and be equal to zero in a special case.

Since the equality $i_1=i_2$ is valid for adiabatic throttling, i.e.

$$u_1+p_1v_1=u_2+p_2v_2, \quad \text{or} \quad u_1-u_2=p_2v_2-p_1v_1,$$

it follows that the external work (displacement work) is done during throttling at the expense of the internal energy of the body.

Due to the presence of intramolecular forces of attraction the internal energy of a real gas consists of two parts: the kinetic component which is only a function of temperature, and the potential component determined by the position of molecules and depending, in addition to temperature, also on volume.

During throttling the potential component of internal energy always increases due to the increase in volume.

If $p_2v_2-p_1v_1$ were equal to zero and, consequently, $u_1-u_2=0$, and the potential component of internal energy increased, the kinetic component

should then decrease. Such throttling will be accompanied by cooling of the gas ($T_2<T_1$).

A real gas shall be cooled still more in the event of positive external work, i.e. when $p_2v_2>p_1v_1$ and $u_2<u_1$. Then, the decrease of temperature shall be due not only to the increase of the potential component of internal energy, but also to the performance of external work by the gas (also at the expense of internal energy).

In practical applications the external work is usually negative, i.e. $p_2v_2<p_1v_1$ or in other words throttling is accompanied by the expenditure of external work consumed to increase the internal energy of the gas ($u_2>u_1$). If the absolute value of the external work, $p_2v_2-p_1v_1$ exceeds the increase of the potential component of internal energy, then the excess work shall be spent to increase its kinetic component and the gas undergoing throttling shall be heated ($T_2>T_1$).

In a special case the absolute value of the difference $p_2v_2-p_1v_1$ may happen to be equal to the increase of the potential component of internal energy, with the kinetic component remaining unchanged and, consequently the temperature of the gas shall also not change ($T_1=T_2$). This case is referred to as gas *inversion* and the temperature of the gas at which inversion takes place is called the *inversion temperature* T_{in}. Consequently, the process of throttling of a real gas at the inversion temperature does not differ outwardly from the throttling of an ideal gas.

If at $p_2v_2<p_1v_1$ the absolute value of external work is lower than the increase of the potential component of internal energy due to throttling, then the kinetic component of internal energy decreases to some extent, i.e. the gas shall be cooled. Hence, with a negative external work there may exist cases of throttling in the course of which the temperature of a real gas increases, remains constant or decreases.

The following throttling effects are distinguished: the *differential temperature* throttling effect during which the pressure and temperature increase by an infinitely small value, and the *integral* throttling effect when the change in pressure and temperature is finite.

If the gas pressure changes by an infinitely small value dp, an infinitely small change in temperature takes place

$$dT_i=\alpha_i\,dp_i \quad \text{or} \quad \alpha_i=(\partial T/\partial p)_i. \tag{14-2}$$

The quantity α_i is called the *differential Joule-Thomson coefficient* and its value can be determined from Eq. (10-20)

$$di=c_p\,dT-\left[T\left(\frac{\partial v}{\partial T}\right)_p-v\right]dp.$$

Since in throttling $di=0$, then

$$c_p\,dT=\left[T\left(\frac{\partial v}{\partial T}\right)_p-v\right]dp,$$

whence

$$\alpha_i=\left(\frac{\partial T}{\partial p}\right)_i=\frac{T\left(\frac{\partial v}{\partial T}\right)_p-v}{c_p} \tag{14-3}$$

and

$$dT=\frac{T\left(\frac{\partial v}{\partial T}\right)_p-v}{c_p}dp. \tag{14-4}$$

Equation (14-3) is true for any substance.

For an ideal gas

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{R}{p}=\frac{v}{T},$$

then the numerator in Eq. (14-3) is equal to

$$T\left(\frac{\partial v}{\partial T}\right)_p-v=\frac{Tv}{T}-v=0$$

and Eq. (14-3) acquires the following appearance

$$\frac{\partial T}{\partial p}=0 \quad \text{or} \quad dT=0 \quad \text{and} \quad T_1=T_2. \tag{14-5}$$

The state of a real gas undergoing adiabatic throttling during which the differential temperature throttling effect changes its sign or the differential Joule-Thomson coefficient is equal to zero is called the *point of inversion.* If before throttling the temperature of a real gas upstream of the throttle is less than the inversion point, the gas shall cool down, but if the initial temperature of the gas is higher than the inversion point, the gas shall be heated.

To find the point of inversion and the conditions in which heating or cooling of a gas shall take place, let us analyze Eq. (14-3).

Throttling of a gas always results in a drop in pressure; dp is negative ($dp<0$); heat capacity c_p is positive. Therefore, the sign of the differential throttling effect and, consequently, the sign of dT depends on the sign of the expression $T(\partial v/\partial T)_p-v$ and is always opposite to it. Then:

(1) with $T(\partial v/\partial T)_p-v>0$ $dT<0$;
(2) with $T(\partial v/\partial T)_p-v=0$ $dT=0$;
(3) with $T(\partial v/\partial T)_p-v<0$ $dT>0$.

The second case can be used to derive the equation of the inversion temperature:

$$T\left(\frac{\partial v}{\partial T}\right)_p-v=0, \quad \text{whence} \quad T_{in}=v\left(\frac{\partial T}{\partial v}\right)_p.$$

The above expression is called the *equation of the curve of inversion.*

Throttling at finite pressure drops is referred to as the *integral throttling effect* or *the integral Joule-Thomson effect.* It is determined by integrating Eq. (14-4)

$$T_2-T_1=\int_{p_1}^{p_2}\frac{T\left(\frac{\partial v}{\partial T}\right)_p-v}{c_p}dp. \tag{14-6}$$

14-4. Throttling of a van der Waals Gas. Inversion Curve

From van der Waals equation

$$(p+a/v^2)(v-b)=RT$$

we find the partial derivative

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{R}{p-\frac{a}{v^2}+\frac{2ab}{v^3}}.$$

Substituting the partial derivative into Eq. (14-4) and making some assumptions, we obtain the following approximate expression valid at $p\to 0$, or at $v\to\infty$

$$dT=\frac{2a/RT-b}{c_p}dp,$$

or the differential throttling effect (or coefficient)

$$\alpha_i=\frac{dT}{dp}=\frac{2a/RT-b}{c_p}, \tag{14-7}$$

where c_p = heat capacity at constant pressure;
a and b = constants of van der Waals equation;
R = gas constant;
T = gas temperature.

With Joule-Thomson differential throttling effect $\alpha_1=0$ we obtain the point of inversion at which

$$\frac{2a}{RT}=b$$

and the inversion temperature

$$T_{in}=\frac{2a}{Rb}.$$

Let us express T_{in} in terms of critical temperature, making use of Eq. (4.3)

$$T_{cr}=\frac{8a}{27Rb}, \quad \text{or} \quad \frac{a}{b}=\left(\frac{27}{8}\right)RT_{cr},$$

then

$$T_{in}=\left(\frac{27}{4}\right)T_{cr}=6.75T_{cr}.$$

At a pressure $p=0$ the inversion temperature of real gases obeying van der Waals equation is 6.75 times greater than critical temperature.

The process of throttling is always associated with a loss of available work. In fact, a throttled gas performs no useful work on the surroundings, and the kinetic energy of the gas does not change, therefore all the work due to expansion of the gas from pressure p_1 to pressure p_2, and the work $p_1v_1-p_2v_2$ done by the surroundings to displace the gas through the throttle is expended to overcome the friction forces and it converts into frictional heat

$$q_{fr}=\int_1^2 p\,dv+p_1v_1-p_2v_2=-\int_{p_1}^{p_2} v\,dp.$$

The frictional work converted into frictional heat is responsible for the increase of gas entropy. The full change of entropy due to throttling is equal to

$$s_2-s_1=-\int_{p_1}^{p_2}\left(\frac{v}{T}\right)dp.$$

More thorough investigations of throttling of a gas obeying the van der Waals equation, and also the data obtained in experimenting with real gases indicate that a real gas has an infinite number of points of inversion that form on a p-T diagram the so-called *curve of inversion.* If the equation of state of a real gas is known, the equation of the curve of inversion can be obtained in the explicit form from the following relationship:

$$T_{in}=v\left(\frac{\partial T}{\partial v}\right)_p.$$

At any pressure substances have two points of inversion: one in the liquid region, and another—in the superheated vapour (gas) region.

The curve of inversion for nitrogen, $T_{in}=f(p)$, shown in Fig. 14-2, is plotted from equation $T\left(\frac{\partial v}{\partial T}\right)_p-v=0$. It can be seen from the diagram that for any pressure there really are two points of inversion at different temperatures. The curve of inversion passes through a maximum.

If the substance considered obeys the van der Waals equation, an analysis of the equation shows that the volume at the maximum point of the curve of inversion is equal to the critical volume, $v_{max}=v_{cr}$; the maximum pressure is nine times the critical pressure, $p_{max}=9p_{cr}$ and the maximum temperature is three times the critical temperature, $T_{max}=3T_{cr}$.

At a pressure $p=0$ the inversion curve intersects the axis of temperature, the x-axis, at two points. For substances obeying the van der Waals equation the temperatures at these two points are as follows: $T_{02}=6.75T_{cr}$ and $T_{01}=0.75T_{cr}$.

The curve of inversion separates the p-T diagram into two regions. All throttling processes initiating inside the inversion curve are accompanied by cooling of the substance undergoing throttling; outside the inversion curve all throttling processes result in heating of the substance. Processes

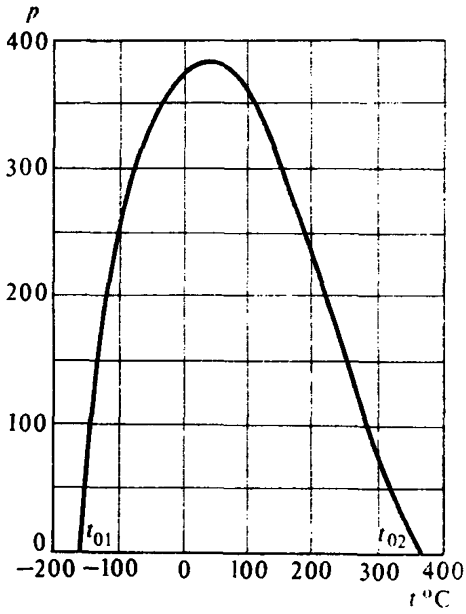


FIG. 14-2

that initiate on the inversion curve correspond to the case of inversion, when $T_1=T_2=T_{in}$.

The theoretical deductions concerning the throttling effect, made on the basis of van der Waals equation of state are fully corroborated qualitatively by experiment, but the quantitative discrepancies are considerable.

14-5. Throttling of Water Vapour (Steam)

A study of the process of throttling of steam can be clearly done through the i-s diagram plotted for steam (Fig. 14-3) on which throttling can be represented arbitrarily by a horizontal line, since such a line only helps to find the parameters of state for the final point and has no physical meaning whatsoever at the intermediate points.

It is clear from the diagram that when superheated steam undergoes throttling (process *1-2*), steam pressure and temperature decrease, and the volume, entropy and the degree of superheat increase. When slightly superheated steam at high pressure undergoes throttling (process *7-8*) the steam first converts into dry saturated, then into wet, further again into dry saturated and again into superheated steam. When boiling liquid is throttled (process *5-6*) it evaporates partly with an increase of the dryness fraction. When wet steam is throttled its dryness fraction increases (process *3-4*).

Throttling is an irreversible process accompanied by an increase of entropy. It is known from the preceding chapters that an increase of entropy

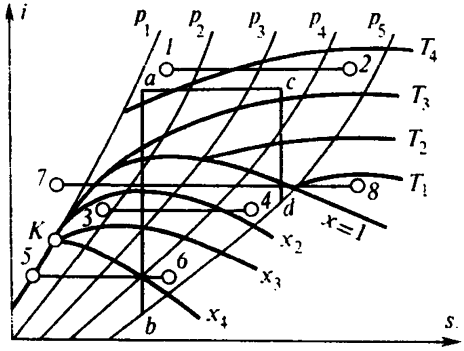


FIG. 14-3

is always associated with a loss of the efficiency of a gas or vapour, which can be easily seen from the diagram in Fig. 14-3. Let steam be throttled from the state *a* to the state *c*. From point *a* and to the pressure p_5 the difference in the enthalpies of the throttled steam is represented by line *ab*; from point *c* the difference in the enthalpies is represented by line *cd* that is considerably smaller than line *ab*, i.e. the efficiency of the steam decreases abruptly. The greater the throttling that steam undergoes the smaller its efficiency.

14-6. Mixing of Gases

The conditions for determining the quantities characterizing a mixture of gases were considered in Chapter III, but the problems involved in the formation of the mixture itself were not dealt with, although the formation of mixtures from gases at different pressures and temperatures is of great importance in engineering.

All methods of mixing gases can be divided into three groups: (1) mixing of gases in a constant volume; (2) mixing of gases in a flow; (3) mixing of gases in filling a vessel.

It is assumed that gases are mixed without heat exchange with the surroundings and that the gases perform no external work.

Mixing in a constant volume. The first method of forming a gas mixture involves several gases at pressures p_1, p_2, p_3, ... and temperatures T_1, T_2, T_3, ... occupying different volumes V_1, V_2, V_3, ... (Fig. 14-4). After the partitions separating the gases are removed the volume of the mixture formed shall be equal to the sum of the volumes of the mixed gases

$$V=V_1+V_2+V_3+\ldots$$

The mass of the gas mixture is equal to the sum of the masses of the mixture components

$$m=m_1+m_2+m_3+\ldots$$

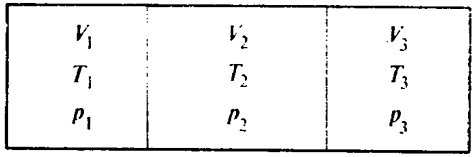


FIG. 14-4

Since in the process of mixing the gases do not perform external work, or work on the surroundings, according to the first law of thermodynamics, the internal energy of the gas mixture is equal, in the special case for ideal gases, to the sum of the internal energies of individual gases before mixing

$$u=u_1+u_2+u_3+\ldots$$

and with $c_v=\text{const}$

$$mc_vT=m_1c_{v1}T_1+m_2c_{v2}T_2+m_3c_{v3}T_3+\ldots,$$

whence

$$T=\frac{m_1c_{v1}T_1+m_2c_{v2}T_2+m_3c_{v3}T_3+\ldots}{mc_v}$$

and

$$T=\frac{m_1c_{v1}T_1+m_2c_{v2}T_2+m_3c_{v3}T_3+\ldots}{m_1c_{v1}+m_2c_{v2}+m_3c_{v3}+\ldots}$$

or

$$T=\frac{g_1c_{v1}T_1+g_2c_{v2}T_2+g_3c_{v3}T_3+\ldots}{g_1c_{v1}+g_2c_{v2}+g_3c_{v3}+\ldots},$$

where g_1, g_2, etc. are the mass fractions of the ideal-gas components of the mixture.

It follows from the equation of state of ideal gases that

$$m_1=\frac{p_1V_1}{R_1T_1};\quad m_2=\frac{p_2V_2}{R_2T_2};\quad m_3=\frac{p_3V_3}{R_3T_3}.$$

Upon substitution of the values of the masses we find that the temperature of the gas mixture is equal to

$$T=\frac{p_1V_1\frac{c_{v1}}{R_1}+p_2V_2\frac{c_{v2}}{R_2}+p_3V_3\frac{c_{v3}}{R_3}+\dots}{\frac{p_1V_1}{T_1}\cdot\frac{c_{v1}}{R_1}+\frac{p_2V_2}{T_2}\cdot\frac{c_{v2}}{R_2}+\frac{p_3V_3}{T_3}\cdot\frac{c_{v3}}{R_3}+\dots}$$

For ideal gases with a constant heat capacity and with a certain degree of accuracy

$$\frac{c_v}{R}=\frac{1}{k-1},$$

therefore, if ideal gases of the *same atomic number* are being mixed $\frac{c_v}{R}$ can be cancelled in the numerator and denominator and we obtain a formula for a mixture of gases of the same atomicity:

$$T=\frac{p_1V_1+p_2V_2+p_3V_3+\dots}{\frac{p_1V_1}{T_1}+\frac{p_2V_2}{T_2}+\frac{p_3V_3}{T_3}+\dots} \tag{14-8}$$

To determine the pressure of a mixture of gases of the same atomic number, let us substitute into Eq. (14-8) the values:

$$T=\frac{pV}{Rm};\quad \frac{p_1V_1}{T_1}=m_1R_1;\quad \frac{p_2V_2}{T_2}=m_2R_2;\quad \frac{p_3V_3}{T_3}=m_3R_3.$$

The resulting equation is as follows

$$\frac{pV}{mR}=\frac{p_1V_1+p_2V_2+p_3V_3+\dots}{m_1R_1+m_2R_2+m_3R_3+\dots}$$

but

$$mR=m_1R_1+m_2R_2+m_3R_3+\dots,$$

therefore

$$p=\frac{p_1V_1+p_2V_2+p_3V_3+\dots}{V} \tag{14-9}$$

or

$$p=\frac{p_1V_1+p_2V_2+p_3V_3+\dots}{V_1+V_2+V_3+\dots} \tag{14-9'}$$

Knowing the temperature, volume and pressure, we can determine all other quantities and parameters of a mixture of gases, making use of the equations for mixtures of ideal gases.

Mixing of gas flows. The mixture of gases forms in this case when several flows of gases meet in one duct and form a single flow, as for instance, the mixing of the exit gases from several boilers in one smoke stack.

Let the first pipeline carry m_1 kg of gas with parameters p_1, V_1, T_1; the second pipeline, m_2 kg of gas with parameters p_2, V_2, T_2; the third pipeline, m_3 kg of gas with parameters p_3, V_3, T_3 (Fig. 14-5).

According to the first law of thermodynamics, when the gases are in adiabatic flow perform no external work, the total energy of the gas flow is equal to the sum of the total energies of the individual flows making up the mixture [Eq. (13-3)]

$$m\left(i+\frac{w^2}{2}\right)=m_1\left(i_1+\frac{w_1^2}{2}\right)+m_2\left(i_2+\frac{w_2^2}{2}\right)+m_3\left(i_3+\frac{w_3^2}{2}\right)+\ldots .$$

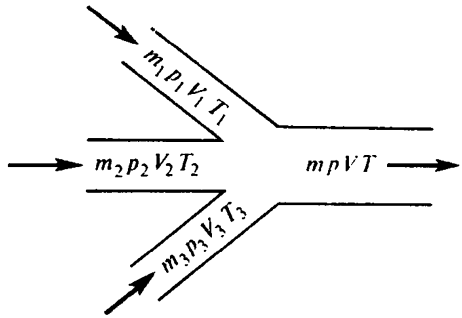


FIG. 14-5

For most practical engineering problems the kinetic energy of flows can be ignored, then we obtain

$$mi+m_1i_1+m_2i_2+m_3i_3+\ldots,$$

or

$$i=g_1i_1+g_2i_2+g_3i_3+\ldots,$$

where g_1, g_2, g_3 are mass fractions.

The derived equation is applicable to ideal gases, real gases and liquids.

Replacing the enthalpy of gas with c_pT, we obtain

$$c_pT=g_1c_{p1}T_1+g_2c_{p2}T_2+g_3c_{p3}T_3+\ldots,$$

and, using Eq. (6.33), we find (at c_p=const) that

$$T(g_1c_{p1}+g_2c_{p2}+g_3c_{p3})=g_1c_{p1}T_1+g_2c_{p2}T_2+g_3c_{p3}T_3,$$

or

$$T=\frac{g_1c_{p1}T_1+g_2c_{p2}T_2+g_3c_{p3}T_3+\ldots}{g_1c_{p1}+g_2c_{p2}+g_3c_{p3}+\ldots}. \qquad (14\text{-}10)$$

Eq. (14-10) is only valid for ideal gases with a constant heat capacity.

The volume of a mixture of ideal gases is determined from the characteristic equation

$$V=\frac{mRT}{p}=\left(\frac{T}{p}\right)(m_1R_1+m_2R_2+m_3R_3+\ldots)=$$

$$=\left(\frac{T}{p}\right)\left(\frac{p_1V_1}{T_1}+\frac{p_2V_2}{T_2}+\frac{p_3V_3}{T_3}+\ldots\right). \qquad (14\text{-}11)$$

Mixing of ideal gases when filling the vessels. A vessel holds m kg of gas with parameters p, V, T. Through a pipeline and valve A another gas flows into the vessel with parameters p_1, V_1, T_1. (Fig. 14-6). Let m kg of the second gas enter the vessel, then the valve closes with the result that the vessel is

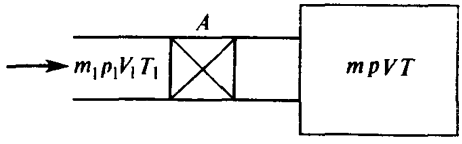


FIG. 14-6

now filled with a mixture of gases of volume V. The process of mixing is irreversible.

According to the first law of thermodynamics, the internal energy of a mixture of ideal gases is equal to the sum of the internal energies of the mixture components

$$mu=m_1u_1+m_2u_2.$$

Assuming that $c_v=\text{const}$, we find the temperature of the mixture

$$c_vT=\left(\frac{m_1}{m}\right)c_{v1}T_1+\left(\frac{m_2}{m}\right)c_{v2}T_2$$

and

$$T=\frac{g_1c_{v1}T_1+g_2c_{v2}T_2}{g_1c_{v1}+g_2c_{v2}}. \qquad (14\text{-}12)$$

Knowing T and V we can determine all parameters of the mixture.

14-7. The Change of Entropy of Ideal Gases Upon Mixing

The entropy of a mixture of ideal gases is equal to the sum of the entropies of the mixture components

$$s_{mix}=g_1s_1+g_2s_2+\ldots+g_ns_n=\sum_1^n g_is_i.$$

It follows from Eq. (6-43) that for a gas with parameters p_{par} and T

$$s_i=c_p\ln\frac{T}{T_{st}}-R\ln\frac{p_{par}}{p_{st}},$$

where T = temperature of the gas mixture;
p_{par} = partial pressure of a component in the mixture that can be determined by formula (3-10).

The second term in the right-side of the equation can be represented as follows

$$R \ln \frac{p_{par}}{p_{st}} = R \ln \frac{pg_i\mu}{p_{st}\mu_i} = R \ln \frac{p}{p_{st}} + R \ln \frac{\mu g_i}{\mu_i},$$

whence

$$(s_{mix})_{p,T} = \sum_1^n g_i \left(c_p \ln \frac{T}{T_{st}} - R_i \ln \frac{p}{p_{st}} \right) - \sum_1^n g_i R_i \ln \frac{\mu g_i}{\mu_i}.$$

The expression in brackets is the entropy of 1 kg of a mixture component that we shall denote by $(s_i)_{p,T}$. The last term is negative since

$$\frac{\mu g_i}{\mu_i} < 1.$$

Consequently,

$$(s_{mix})_{p,T} = \sum_1^n g_i (s_i)_{p,T} + \sum_1^n g_i R_i \ln \frac{\mu_i}{\mu g_i},$$

or, using the formula (3-2), we obtain

$$(s_{mix})_{p,T} = \sum_1^n g_i (s_i)_{p,T} + \sum_1^n g_i R_i \ln \frac{1}{r_i}. \qquad (14\text{-}13)$$

From Eq. (14-13) it follows that if several different gases are mixed at parameters p, T of the mixture, the entropy of the gas mixture shall not be equal to the sum of the entropies of individual components, taken at the mixture pressure and temperature, but shall be larger by some quantity, equal to the change of entropy upon mixing.

Just like other methods of mixing, the mixing of gases in a flow is an irreversible process that is always accompanied by an increase in entropy. This phenomenon can be traced to the fact that in the course of mixing the gas expands without producing work. In addition, the mixing of gases in one vessel is accompanied by their diffusion which is an irreversible process. When, on the contrary, a gas mixture has to be separated into individual components, a minimum amount of work must be expended, equal to the efficiency loss $T_0 \Delta s$ due to mixing of gases (see example 14-6).

Typical Questions and Examples to Chapter Fourteen

1. Which process is referred to as throttling and where is that process encountered?
2. Which quantities change and which remain constant beyond a constriction placed in a flow?

3. Write down the equation of adiabatic throttling.
4. Why cannot the process of throttling be called isenthalpic?
5. How does the temperature of an ideal gas change upon throttling?
6. Joule-Thomson effect and its equation.
7. What is meant by the differential and integral throttling effects?
8. Throttling of real gases.
9. What is meant by the point and temperature of inversion?
10. The differential Joule-Thomson coefficient for gases obeying the van der Waals equation.
11. Show how is the inversion temperature of real gases determined.
12. When and under what conditions does the temperature of a real gas rise, fall or remain unchanged upon throttling?
13. Investigation of steam throttling on the *i-s* diagram.
14. The change in the efficiency of steam upon throttling.
15. Give the definition of the temperature and pressure of a gas mixture at a constant volume.
16. The temperature of a mixture of gases upon filling a vessel.
17. The temperature and volume of a gas mixture upon mixing in a flow.
18. Explain the reason for the change of entropy in mixing and write down the formula for the entropy of a mixture of gases.

Example 14-1. One kg of superheated steam at a pressure $p_1=100$ bar is at a temperature $t_1=530$ °C.; in the first case the steam flows into a turbine where it expands adiabatically to a final pressure $p_2=0.05$ bar. Upon expansion, due to a change in its external kinetic energy, the steam performs work, equal numerically to the change of enthalpy.

In the second case the steam is first throttled in a valve to the intermediate pressure $p_1'=3$ bar, then the steam expands again adiabatically in the steam turbine to the same final pressure.

Determine the temperature of steam beyond the valve, the increase of entropy and the loss of useful work due to throttling.

The initial parameters of the steam are: $i_1=3450$ kJ/kg and $s_1=6.7$ kJ/kg·deg. Drawing on the *i-s* diagram a horizontal line till it intersects the isobar $p_1'=3$ bar, we find the temperature of steam at the end of throttling, $t_1'=483$ °C. From the same diagram we find that upon adiabatic expansion from the initial state to the pressure $p_2=0.05$ bar steam enthalpy $i_2=2040$ kJ/kg; the decrease of enthalpy in the process is equal to $h_1=i_1-i_2=3450-2040=1410$ kJ/kg. With adiabatic expansion the loss of enthalpy due to throttling is $h_2=i_1-i_2''=3450-2530=920$ kJ/kg. From this it follows that the loss of efficiency of steam $\Delta h=1410-920=490$ kJ/kg or, in per cent

$$\Delta h=\frac{1410-920}{1410}\times 100=35 \text{ per cent.}$$

The entropy of throttled steam $s_2=8.3$ kJ/kg·deg. The process of throttling

is a typical irreversible process and is always accompanied by an increase in entropy. In the conditions given, entropy increases by

$$s_2 - s_1 = 8.3 - 6.7 = 1.6 \text{ kJ/kg·deg.}$$

Example 14-2. Three vessels, interconnected by piping, contain: oxygen with $V_1 = 1.5$ m³ at $T_1 = 300$ K and $p_1 = 2$ bar; air with $V_2 = 3$ m³ at $T_2 = 350$ K and $p_2 = 4$ bar; carbon oxide with $V_3 = 5.5$ m³ at $T_3 = 400$ K and $p_3 = 6$ bar. Determine the temperature and pressure of the mixture of gases after the valves have been opened.

The temperature of the gas mixture is determined by Eq. (14-8)

$$T = \frac{p_1V_1 + p_2V_2 + p_3V_3}{p_1V_1/T_1 + p_2V_2/T_2 + p_3V_3/T_3} = \frac{2\times1.5 + 4\times3 + 6\times5.5}{2\times1.5/300 + 4\times3/350 + 6\times5.5/400} = 380 \text{ K.}$$

The pressure of the gas mixture is found from Eq. (14-9)

$$p = \frac{p_1V_1 + p_2V_2 + p_3V_3}{V_1 + V_2 + V_3} = \frac{2\times1.5 + 4\times3 + 6\times5.5}{1.5 + 3 + 5.5} = 4.8 \text{ bar}$$

Example 14-3. Gases, flowing from three pipelines, mix in a duct: 2 kg of air at $p_1 = 2$ bar and $T_1 = 500$ K; 3 kg of carbon dioxide at $p_2 = 2$ bar and $T_2 = 400$ K; 5 kg of oxygen at $p_3 = 3$ bar and $T_3 = 300$ K. Assuming the heat capacities to be constant, determine the temperature and specific volume of the gas mixture at a pressure of 1 bar.

The heat capacity of the mixture of gases is

$$c_p = g_1c_{p1} + g_2c_{p2} + g_3c_{p3} = 0.2\times1.15 + 0.3\times0.86 + 0.5\times1.15 =$$
$$= 1.063 \text{ kJ/kg·deg.}$$

The temperature of the mixture of gases

$$T = \frac{g_1c_{p1}T_1 + g_2c_{p2}T_2 + g_3c_{p3}T_3}{g_1c_{p1} + g_2c_{p2} + g_3c_{p3}} = \frac{0.23\times500 + 0.258\times400 + 0.575\times300}{1.063} = 391 \text{ K.}$$

The gas constant of the mixture is equal to

$$R = g_1R_1 + g_2R_2 + g_3R_3 = 0.2\times287 + 0.3\times189 + 0.5\times260 = 244 \text{ J/kg·deg.}$$

The specific volume of the gas mixture amounts to

$$v = \frac{RT}{p} = \frac{244\times391}{1\times10^5} = 0.955 \text{ m}^3\text{/kg.}$$

Example 14-4. A vessel of 5 m³ capacity contains oxygen at a pressure $p_1 = 3$ bar and $T_1 = 320$ K; 0.6 m³ of carbon dioxide is delivered into the vessel through a pipeline at $p_2 = 12$ bar and $T_2 = 400$ K. Assuming the heat capacity to be constant, determine the parameters of state of the gas mixture.

The mass of oxigen

$$m_{O_2} = \frac{pV}{RT} = \frac{3\times10^5\times5}{259.82\times320} = 18 \text{ kg.}$$

The mass of carbon dioxide

$$m_{CO_2}=\frac{pV}{RT}=\frac{12\times10^5\times0.6}{189\times400}=9.5 \text{ kg.}$$

The mass fraction of oxygen in the mixture

$$g_1=\frac{18}{27.5}=0.655,$$

and its heat capacity amounts to

$$c_{v1}=\frac{20.93}{32}=0.653 \text{ kJ/kg·deg.}$$

The mass fraction of carbon dioxide $g_2=0.345$, and its heat capacity

$$c_{v2}=\frac{29.31}{44}=0.665 \text{ kJ/kg·deg.}$$

The temperature of the gas mixture is

$$T=\frac{g_1c_{v1}T_1+g_2c_{v2}T_2}{g_1c_{v1}+g_2c_{v2}}=\frac{0.655\times0.653\times320+0.345\times0.665\times400}{0.655\times0.653+0.345\times0.665}=348 \text{ K.}$$

The gas constant of the gas mixture is equal to

$$R=g_1R_1+g_2R_2=0.655\times259.82+0.345\times189=235.4 \text{ J/kg·deg.}$$

The pressure of the mixture of gases is equal to

$$p=\frac{mRT}{V}=\frac{27.5\times235.4\times348}{5\times10^5}=4.5 \text{ bar.}$$

Example 14-5. Determine the entropy of 1 kg of a gas mixture consisting of nitrogen and oxygen kept at a pressure $p=0.5 \frac{\text{MN}}{\text{m}^2}$ or $p=5$ bar and a temperature $t=400$ °C. The mass fractions of nitrogen and oxygen in the mixture are: $g_{N_2}=0.4$; $g_{O_2}=0.6$. Assume the gases to be ideal ones.

Assume also that the entropies of nitrogen and oxygen are equal to zero at $p_0=1$ bar and $t_0=0$ °C. The heat capacity of the gases is variable.

The entropy of a mixture is equal to the sum of the entropies of individual gas components plus the change in entropy due to mixing [Eq. (14-13)]

$$(s_{mix})_{p,t}=g_1(s_1)_{p,t}+g_2(s_2)_{p,t}+g_1R_1\ln\frac{1}{r_1}+g_2R_2\ln\frac{1}{r_2};$$

$$(s_1)^{N_2}_{p,t}=g_1\left(c_{p1}\ln\frac{T}{T_0}-R_1\ln\frac{p}{p_0}\right)=$$

$$=0.4\left(1.0823\times2.3\log\frac{673}{273}-0.2968\times2.3\log\frac{5}{1}\right)=+0.259 \text{ kJ/kg·deg;}$$

$$(s_2)^{O_2}_{p,t}=g_2\left(c_{p2}\ln\frac{T}{T_0}-R_2\ln\frac{p}{p_0}\right)=$$

$$=0.6\left(1.0237\times2.3\log\frac{673}{273}-0.2598\times2.3\log\frac{5}{1}\right)=+0.387 \text{ kJ/kg·deg.}$$

The change in entropy due to mixing is equal to

$$\Delta s_{mix}=g_1R_1\ln\frac{1}{r_1}+g_2R_2\ln\frac{1}{r_2}=0.4\times0.2968\times0.433+0.6\times0.2598\times$$

$$\times0.567=1.4\ \text{kJ/kg·deg}.$$

At the given parameters the entropy of 1 kg of mixture is

$$(s_{mix})_{p,\,t}=(s_1)^{N_2}_{p,\,t}+(s_2)^{O_2}_{p,\,t}+\Delta s_{mix}=0.259+0.387+1.4=2.046\ \text{kJ/kg·deg}.$$

The volume fraction of each gas component is determined in the following way:

$$r_i=\left(\frac{\mu}{\mu_i}\right)g_i,\quad \mu=\frac{1}{\frac{g_1}{\mu_1}+\frac{g_2}{\mu_2}}.$$

Knowing μ of the mixture and the mass fraction, it is easy to determine the volume fraction of each gas component.

Example 14-6. At a temperature of 20 °C determine the minimum theoretical work required to separate 1 kg of a gas mixture consisting of 30 fractions by volume of carbon dioxide and 70 fractions by volume of nitrogen, assuming the gases to be ideal ones. The minimum work to spend to separate the gases shall be equal to the loss of efficiency upon mixing

$$l=T_0\Delta s,$$

where Δs is the change of entropy in mixing, equal to

$$\Delta s=g_1R_1\ln\frac{1}{r_1}+g_2R_2\ln\frac{1}{r_2},$$

(where g and r are the mass and volume fractions of the gases);

$$\Delta s=0.402\times0.189\times2.3\ \log\frac{1}{0.3}+0.598\times0.2968\times2.3\ \log\frac{1}{0.7}=$$

$$=0.1548\ \text{kJ/kg·deg};$$

$$\mu=r_1\mu_1+r_2\mu_2=0.3\times44+0.7\times28=32.8;$$

$$g_1=r_1\left(\frac{\mu_1}{\mu}\right)=0.3\left(\frac{44}{32.8}\right)=0.402;\quad g_2=0.7\left(\frac{28}{32.8}\right)=0.598.$$

The minimum work required to separate the gases is

$$l=T_0\Delta s=293\times0.1548=45.4\ \text{kJ/kg}.$$

CHAPTER FIFTEEN

HUMID AIR

15-1. General Concepts. Absolute Humidity, Moisture Content and Relative Humidity of Air

A mixture of dry air (not containing any molecules of water) and water vapour is referred to as *humid air.*

Humid air finds wide application in engineering, therefore it is very important to know its properties. The physical properties of humid air make it close to an ideal gas.

At a given pressure and temperature humid air may contain different amounts of water vapour. A mixture consisting of dry air and saturated water vapour is called *saturated humid air.* The partial pressure of water vapour in this mixture is equal to the saturation pressure at the given temperature. The quantity of water vapour contained in each cubic metre of such air is equal numerically to the density of dry saturated vapour ϱ'' (kg/m^3).

According to Dalton's law, the total pressure of humid air is equal to the sum of the partial pressures of humid-air components, dry air and water vapour, i.e.

$$p=p_a+p_v, \tag{15-1}$$

where p_a = partial pressure of dry air;
p_v = partial pressure of water vapour.

The mass of water vapour contained in 1 m^3 of humid air, equal numerically to the density of water vapour, ϱ_v, at a partial pressure p_v, is called the *absolute humidity.* If at a constant temperature t the air humidity is increased, the density of water vapour shall increase. But if the temperature of humid air is below the saturation temperature of water vapour at the given pressure, the maximum density of water vapour shall be the density of dry saturated vapour at a partial pressure below the pressure of the dry air-saturated water vapour mixture. In this limiting state humid air is a mixture of dry air and dry saturated water vapour.

However, the temperature of humid air can possibly be higher or equal to the saturation temperature of water vapour at the pressure of the mixture. Then the process of saturation of humid air with water vapour will continue until it consists of only dry saturated water vapour (when $t_{mix}=t_s$) or of superheated vapour (when $t_{mix}>t_s$).

Let us consider humid air on a p-v diagram at any pressure p and various temperatures (Fig. 15-1). Let us plot the specific volumes of water vapour along the abscissa; the reciprocals of the specific volumes are used to

measure the density of water vapour, and—its absolute humidity with respect to humid air.

From point *1* (at a pressure $p=p_s$), determining the state of dry saturated vapour, we draw the isotherm t_{12}. If humid air is considered at the temperature $t_{34}<t_{12}$, it will be saturated when its vapour component shall be dry saturated, i.e. when for the humid air there shall be a maximum value of absolute humidity. To this value corresponds the point *3* of dry saturated vapour (the appearance of mist is not considered here).

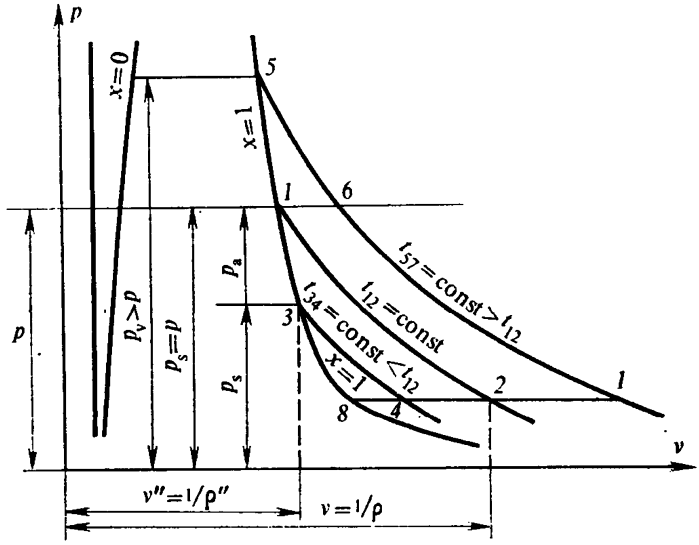


FIG. 15-1

It is clear from the *p-v* diagram that at temperatures below t_{12} saturated air is a mixture of dry air and saturated vapour. In the general form $p=p_a+p_v$, where p_a is the partial pressure of dry air, and p_v—the partial pressure of the saturated vapour component of humid air. At a temperature T_{12} humid air shall be saturated when the vapour is in the state characterized by point *1*. Humid air then consists only of dry saturated vapour, since $p_v=p$, and $p_a=0$. At a pressure p and temperature $t_{57}>t_{12}$ humid air shall be saturated when the state of vapour is characterized by point *6*. The vapour shall then be superheated and saturated air only consists of superheated vapour, since the pressure $p_v=p$ and $p_a=0$.

Humid air that does not contain a maximum possible amount of water vapour at a given pressure and temperature is referred to as *unsaturated*. Unsaturated humid air is a mixture of dry air and superheated vapour, as can be seen from the *p-v* diagram (Fig. 15-1). The partial pressure of the superheated vapour in the mixture will be lower than the saturation pressure at the given temperature. The quantity of superheated vapour in 1 m³ of

air is equal numerically to the density of superheated vapour, but is less than the numerical magnitude of the density of dry saturated vapour. By cooling air and, consequently, superheated vapour at some constant pressure p, for instance, along line *7-8*, the superheated vapour can be brought to the saturation state characterized by point *8*. This state shall be reached when the temperature of air becomes equal to the saturation temperature of water vapour at the given partial pressure. This temperature is referred to as the *dew point*.

The ratio of the mass of vapour, m_v, contained in humid air to the mass of dry air, m_a, in the dry air-vapour mixture is called the *moisture content of air*, measured in units of kilogram per kilogram (kg/kg) or in gram per kilogram (g/kg)

$$d=\frac{m_v}{m_a}, \text{ or } d=\frac{\varrho_v}{\varrho_a}. \tag{15-2}$$

It follows that the quantity d measures the mass of vapour contained in 1 kg of dry air or in $(1+d)$ kg of humid air. The moisture content d can be determined in the following manner. The equations of state for 1 kg of dry air and water vapour components of V m^3 of humid air, are as follows:

$$p_aV=m_aR_aT \text{ and } p_vV=m_vR_vT.$$

Let us divide the two equations termwise

$$\frac{p_a}{p_v}=\frac{m_aR_a}{m_vR_v}=\frac{m_a\times 287.04}{m_v\times 461.6}=\frac{0.622}{d}. \tag{15-3}$$

Substituting into Eq. (15-3) the value of p_a from Eq. (15-1), we find the magnitude of the moisture content

$$d=0.622\frac{p_v}{(p-p_v)}. \tag{15-4}$$

It is clear from Eq. (15-4) that an increase in the partial pressure of vapour, p_v, causes an increase of the moisture content d.

The maximum moisture content depends on the temperature and pressure of humid air. If the temperature of humid air is lower than the saturation temperature of water vapour at the pressure of the dry air-vapour mixture, then the maximum moisture content is determined by the ratio of the pressure of saturated water vapour at the temperature of the dry air-vapour mixture to air partial pressure.

If the temperature of humid air is higher or equal to the saturation temperature of water vapour at the pressure of the dry air-vapour mixture, then the maximum moisture content is equal to infinity, since then humid air shall only consist of dry saturated, or superheated, water vapour.

The ratio of the actual absolute humidity of unsaturated air to the maximum possible absolute humidity of air at the same temperature is called the *relative humidity* and denoted by φ

$$\varphi=\frac{\varrho_v}{\varrho_{max}}. \tag{15-5}$$

The relative humidity of air may vary from $\varphi=0$ (dry air) to $\varphi=1$ (air saturated with mosture).

It follows from Clapeyron's equation that

$$p_v=R_v\varrho_v T; \quad p_{max}=R_v\varrho_{max}T,$$

whence

$$\varphi=\frac{p_v}{p_{max}}. \tag{15-6}$$

If air is considered to be an ideal gas, its absolute humidity is equal numerically to the ratio of the partial pressure of the water vapour contained in the air to the maximum possible pressure of water vapour at the dry air-vapour mixture temperature.

If the temperature of humid air is below or equal to the saturation temperature of water vapour at the humid air pressure, then p_{max} is equal to the partial pressure of saturated vapour, p_v, at the mixture temperature. But if the temperature of humid air is higher than the saturation temperature at the mixture pressure, then p_{max} is equal to the pressure of humid air, p.

Equations (15-4) and (15-6) can be used to obtain an expression relating the moisture content to the relative humidity

$$\varphi=\frac{d}{0.622+d}\cdot\frac{p}{p_{max}}.$$

It follows from the above expression that in the region where humid air temperature is higher than the saturation temperature of water vapour at the pressure of the dry air-water vapour mixture, i.e. when $p_{max}=p$, relative humidity only depends on the moisture content and shall not change at $d=$const.

Lowering the temperature of unsaturated air ($\varphi<1$) at a constant pressure, it can be brought to the state of saturation ($\varphi=1$). This shall take place when air temperature becomes equal to the temperature of dry saturated vapour at its given partial pressure in the air. Further cooling of humid air results in that water begins to separate out of it in the form of mist or dew. The temperature at which saturation of the humid air sets in (at $\varphi=1$) is called the *dew point* and is denoted by t_d. The dew point t_d is determined with the aid of a hygrometer, and the partial pressure of water vapour—by means of a psychrometer. Knowing the dew point and air temperature, it is possible to determine from the steam tables the pressure p_v and p_{max}, and the formula (15-6) can then be used to calculate the relative humidity of air

$$\varphi=\frac{p_v}{p_{max}}.$$

The simplest condensing hygrometer consists of a thin-walled metallic cylindrical vessel whose walls are thoroughly polished. The vessel is filled with ether. When air is pumped through the ether, a fraction of the ether evaporates and its temperature drops. The temperature of the ether is equal

practically to the temperature of cylinder walls. The ether is cooled until dew appears on the polished metal surface of the vessel. At that moment the temperature of the ether is registered and that temperature shall correspond to the dew point. The appearance of dew evidences the transition of the layer of air adjoining the walls of the vessel into the state of saturation. Such determination of the partial pressure and subsequently of relative humidity with the aid of a hygrometer cannot be assumed to be sufficiently accurate.

Relative humidity and the moisture content of humid air are determined more precisely with the aid of a psychrometer. The instrument consists of two thermometers: a wet-bulb thermometer and a dry-bulb one. The bulb of the wet-bulb thermometer is covered with a thin layer of cloth which is continuously dripping with water. If the air is unsaturated, water shall evaporate from the surface of the cloth covering the wet bulb and the thermometer shall indicate a temperature lower than that read off dry-bulb thermometer. It is clear that the dry-bulb thermometer shall indicate the actual temperature of humid air, t_{db}, and the wet-bulb thermometer—the temperature of the evaporating water, t_{wb}. Knowing the psychrometric temperature difference, it is possible to determine with the aid of special tables the relative humidity and the moisture content of air.

15-2. Density, Gas Constant and Enthalpy of Humid Air

The density of humid air is equal to the sum of the densities of water vapour and dry air, taken at their partial pressures and the temperature of the dry air-water vapour mixture

$$\varrho = \varrho_v + \varrho_a. \tag{15-7}$$

The density of humid air is determined by equations

$$\varrho = \frac{p}{RT}; \quad \varrho = \varrho_v r_v + \varrho_a r_a.$$

The gas constant of humid air can be determined from Eqs. (3-4), (3-5) and (3-6)

$$R = \frac{8314.2}{\mu_{mix}} = \frac{8314.2}{\mu_a r_a + \mu_v r_v}.$$

The enthalpy of humid air is equal to the sum of the enthalpies of dry air and water vapour. It is more convenient to reduce the enthalpy of humid air to 1 kg of dry air or to $(1+d)$ kg of humid air.

The enthalpy of $(1+d)$ kg of humid air is equal to

$$i = i_a + di_v. \tag{15-8}$$

The enthalpy of 1 kg of dry air, expressed in units of kJ per kilogram (kJ/kg), is equal numerically to its temperature t °C, since the heat capacity of dry air at constant pressure is approximately equal to 1 kJ/kg·deg. At

low pressures the enthalpy of 1 kg of dry air can be determined by the empirical formula

$$i_v = 2490 + 1.97t_s,$$

then the enthalpy of humid air shall be

$$i = t + (2490 + 1.97t_s)d.$$

15-3. The *i-d* Diagram for Humid Air

The properties of humid air are usually determined graphically with the aid of the *i-d* diagram suggested by prof. L. K. Ramzin in 1918 (Fig. 15-2).

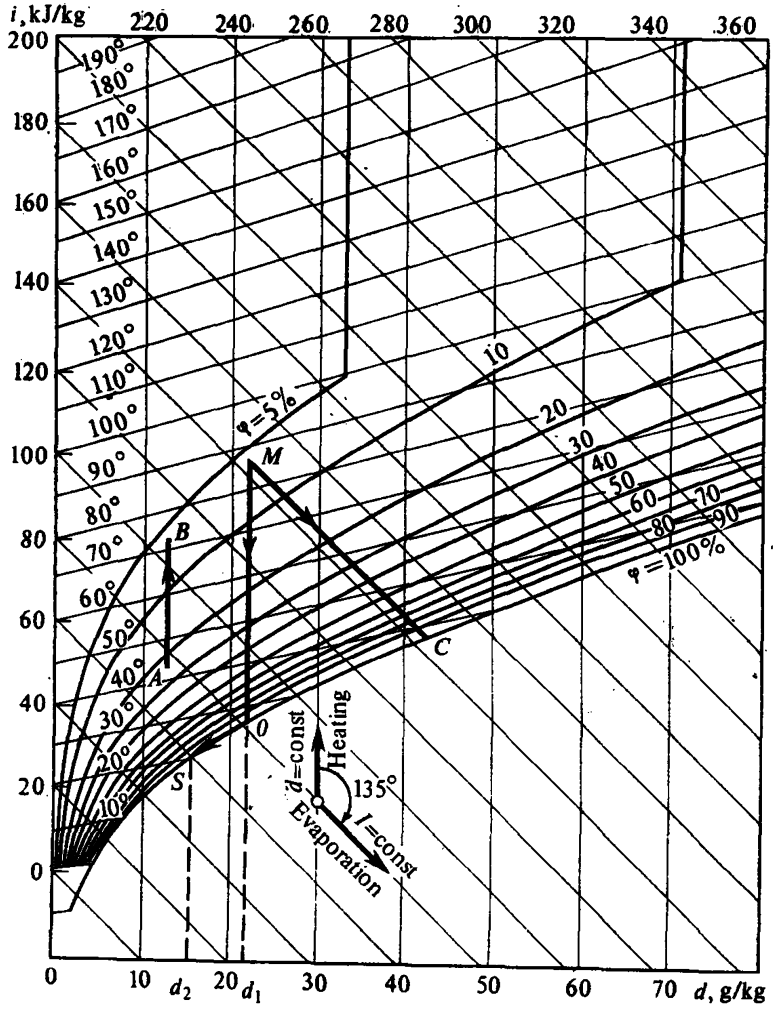


FIG. 15-2

On this diagram enthalpy i, kJ/kg, is plotted along the vertical axis, and the moisture content d, g/kg of dry air—along the horizontal axis. To ensure a more convenient arrangement of various lines on the diagram, the axes of coordinates are arranged at an angle of 135°, the ordinate being vertical.

Thus, moisture content (d) lines are vertical and enthalpy i is represented by inclined straight lines. The following lines are drawn on the *i-d* diagram: lines of constant enthalpies (straight lines making an angle of 45° with the ordinate); lines of constant moisture contents (straight lines running parallel to the ordinate); lines of constant humid air temperatures; lines of relative air humidity.

The *i-d* diagram is usually plotted for a barometric pressure of 0.9930 bar, but it can be used with sufficient accuracy for other pressures close to the basic one. With t and φ known, the *i-d* diagram permits determination of i and d, and d can be used to determine p_v. In addition, the *i-d* diagram can be used to determine for each state of humid air the dew point, i.e. the temperature at which humid air shall be saturated with water vapour $\varphi = 100$ per cent.

Humid air is heated at a constant moisture content, i.e. $d = \text{const}$. On the *i-d* diagram the heating process is represented by the vertical straight line *AB*. The process of cooling humid air also proceeds at $d = \text{const}$ and is represented on the diagram by the straight line *MO*. Such representation of the process on the *i-d* diagram is valid only for the state in which air is fully saturated, i.e. when $\varphi = 100$ per cent. Further cooling causes supersaturation of the air with moisture and the moisture shall fall out of it as dew.

Condensation may be arbitrarily assumed to proceed along the line $\varphi = 100\%$. For instance, the amount of water resulting from the condensation from point *O* to point *S* per kg of dry air is equal to the difference in the moisture contents $d_1 - d_2$. In conditions of constant pressure an ideal process of saturation of air with moisture proceeds at a constant enthalpy of the humid air ($i = \text{const}$) and is depicted on the *i-d* diagram by line *MC*. By ideal is meant here a process during the development of which all the heat is spent to evaporate the moisture, i.e. the loss of heat to the surroundings and the expenditure of heat to raise the liquid temperature are ignored.

In this case the heat transferred from the humid air and spent to evaporate the moisture returns again to the humid air together with the vapour, i.e. the total heat balance is zero.

In the course of moisture evaporation the quantity of dry air in the air-water vapour mixture does not change, and hence, nor does the enthalpy of humid air, calculated per 1 kg of the dry air contained in the air—water vapour mixture.

The *i-d* diagram enables the determination of the dew point. For this purpose from the point characterizing a given state of the air it is necessary to draw a vertical line intersecting with the line $\varphi = 100\%$, and the isotherm

passing through that point of intersection shall determine the dew point (point *O*).

In 1950, G. A. Mikhailovskii suggested an *i-s* diagram for humid air that finds application in special calculations, for instance, of gas turbines, ejectors, etc. Calculations with the aid of the *i-s* diagram give an error of 4 to 6 per cent.

Typical Questions and Examples to Chapter Fifteen

1. What is meant by humid air?
2. What is meant by saturated and unsaturated humid air?
3. Dalton's law as applied to humid air.
4. What is meant by absolute humidity?
5. What is meant by the moisture content of humid air?
6. Name the limits in which moisture content can change.
7. What is called the relative humidity of air?
8. What is meant by the dew point?
9. How is the density of humid air determined?
10. How is the gas constant of humid air determined?
11. How is the enthalpy of humid air determined?
12. Describe the *i-s* diagram for humid air.
13. What kind of lines are plotted on the *i-s* diagram?
14. How are the main processes taking place in humid air represented on the *i-s* diagram?

Example 15-1. Macaroni are dried with air at $t_1=25$ °C and a relative humidity $\varphi=50\%$. In an air heater air is heated to $t_2=90$ °C and directed to the dryer which the air leaves at a temperature $t_3=35$ °C. Determine the final moisture content of air, the amounts of heat and air spent per 1 kg of evaporated moisture. The process of saturation of humid air is assumed to be ideal.

On the *i-s* diagram, at the point where the lines $t_1=25$ °C and $\varphi=50\%$ intersect, we find the point at which we determine the initial moisture content $d_1=10.0$ g/kg and enthalpy $i_1=50.0$ kJ/kg. Since the air is heated at a constant moisture content, $d=\text{const}$, we find at the intersection with the isotherm $t_2=90$ °C the point that characterizes the state of the heated air at the outlet from the air heater. From that point we draw a line at $i=\text{const}$ until it intersects with the isotherm $t_3=35$ °C. This point of intersection characterizes the state of the air at the outlet from the dryer. For this point we find: $d_3=32.0$ g/kg; $i_2=i_3=117.5$ kJ/kg and $\varphi_2=90\%$. Hence, in the course of heating 1 kg of dry air the amount of evaporated moisture is $d_3-d_1=32.0-10.0=22.0$ g/kg. Therefore, to evaporate 1 kg of moisture, it is necessary to spend $1000/22=45.5$ kg of hot dry air. The amount of heat spent in the air heater to heat 1 kg of air amounts to $i_2-i_1=117.5-50=$ $=67.5$ kJ/kg. The consumption of heat per 1 kg of evaporated moisture shall amount to $q=67.5\times45.5=3070$ kJ/kg.

CHAPTER SIXTEEN

COMPRESSORS

16-1. Single-Stage Compressor

A *compressor* is a machine capable of compressing various gases. Compressors have found wide application in modern engineering. They are used in the chemical industry, machine-building, metallurgy, railroads, aviation, gas-turbine plants, and also in the food industry for refrigerators, etc.

Depending on design and principle of operation, all compressors can be subdivided into two groups: *reciprocating* (piston) and *rotary* (centrifugal) compressors. In spite of the difference in the principles involved in compressing a gas in these compressors, and the difference in their designs, the thermodynamics of the process of compression proceeding in them is the same for both types of machines. The processes occurring in compressors are described by the same equations. That is why, to investigate and analyze the processes taking place in any machine to compress a gas, let us consider the performance of the simplest single-stage reciprocating, or piston, compressor, in which all the phenomena involved have been properly studied.

The compressor (Fig. 16-1) consists of cylinder *1* with a jacket in which cooling water circulates, and piston *2*, linked by means of a crank gear with an electric motor or other source of mechanical work. The cylinder cover houses in special boxes two valves: intake (suction) valve *3* and discharge valve *4*, opening automatically as the cylinder pressure changes.

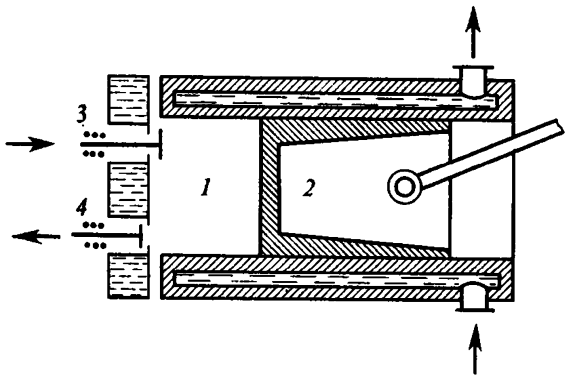


FIG. 16-1

The working process of the compressor is realized during one revolution of the shaft or two strokes of the piston. When the piston travels to the right the intake valve opens and the working medium, gas, enters and fills the cylinder. During the return stroke of the piston the intake valve closes, the gas is compressed to the given pressure and discharged into a receiver from which the compressed gas is dispensed to consumers. Then the indicated processes repeat themselves. The magnitude of the final pressure is determined by the spring mounted on the discharge valve.

The main purpose of thermodynamic calculations of a compressor is to determine the amount of work expended to produce 1 kg of compressed gas and, consequently, the power of the driving engine.

Let us consider a theoretical single-stage compressor, making the following assumptions. The geometrical volume of the compressor cylinder is equal to the piston displacement (there is no clearance or dead space in the cylinder). No work is lost due to friction between the piston and the cylinder face and throttling in the valves. The gas is admitted into the cylinder and is discharged into the receiver at a constant pressure.

The theoretical indicator diagram of the process of producing compressed gas in the compressor is shown in Fig. 16-2.

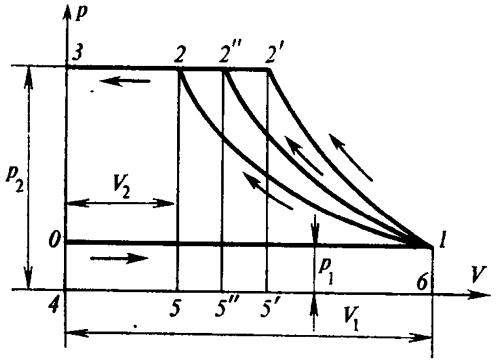


FIG. 16-2

As the piston travels from the left to the right the intake valve *3* opens and the cylinder is being filled with the handled gas at a constant pressure p_1. This process is represented on the indicator diagram by line *0-1* and is referred to as the *suction* (admission) *line*. During the return stroke of the piston from the right to the left intake valve *3* closes and the gas filling the cylinder is being compressed. As soon as the given pressure is reached the entire compressed gas is discharged from the cylinder at a constant pressure through the open discharge valve *4* into a receiver for storage or is delivered to consumers. The curve *1-2* is called the *compression process*. Line *2-3* is referred to as the *discharge line*. It should be noted that the suction line *0-1* and the discharge line *2-3* do not depict thermodynamic processes since the state of the working medium remains unchanged, and only its quantity

changes. At the beginning of the next piston stroke, from the left to the right, the discharge valve closes, cylinder pressure p_2 drops theoretically instantaneously to p_1, the intake valve opens and the entire process of gas compression is repeated.

The work l spent to produce 1 kg of compressed gas (ignoring friction) on condition that all the processes involved are reversible and there is no increase in the kinetic energy of the gas is determined from the following expression:

$$l=p_1v_1-p_2v_2+\int_{v_1}^{v_2} p\,dv,$$

where p_1v_1 = work done by the surrounding medium when the cylinder is being filled with the gas;

p_2v_2 = work spent to displace (discharge) the gas;

$\int_{v_1}^{v_2} p\,dv$ = work spent to compress the gas.

Since $p_1v_1-p_2v_2=\int_2^1 d(pv)$, then

$$l=\int_1^2 [-d(pv)+p\,dv]=-\int_1^2 v\,dp. \qquad (16\text{-}1)$$

In the presence of friction the work expended to drive the compressor (real work) will be greater than the theoretical work by the magnitude of the work spent to overcome friction forces, q_{fr}, and shall amount to

$$l_{real}=-\int_{p_1}^{p_2} v\,dp-q_{fr}. \qquad (16\text{-}2)$$

The area confined between the compression line and the ordinate, then represents but a fraction of the work spent.

If during the process of compression an amount heat q_{real} is transferred from the compressed gas, then, in accordance with the first law of thermodynamics,

$$l_{real}=-(i_2-i_1-q_{real}). \qquad (16\text{-}3)$$

Depending on the conditions under which heat is transferred from the working medium (gas) to the walls of the cylinder, the gas can be compressed in the machine along isotherm *1-2*, adiabat *1-2'* and polytrope *1-2''*. Compression following each of the three processes yields on the indicator diagram a different in size area representing the work spent.

Compression along isotherm *1-2* gives the smallest area *01230* and smallest expenditure of work. All the energy transferred in the form of work is rejected from the gas in the form of heat. Compression along adiabat *1-2'* yields the largest area *012'30* and the greatest expenditure of work, with all the energy added in the form of work being spent to change the enthalpy of the gas. With polytropic compression the amount of work spent acquires an intermediate value.

To reduce the work of compression, the process of compression should be made almost isothermal for which purpose heat must be transferred from the gas being compressed in the cylinder, which is ensured by cooling the external surface of the cylinder with water flowing through the cylinder jacket formed by the hollow cylinder walls. Cooling of the cylinder permits compression of the gas to higher pressures and then the resulting high rate of heat transfer between the working medium and cylinder walls makes it possible to realize polytropic compression with a mean exponent, equal to $n=1.18-1.2$. The walls of cylinders of small-capacity compressors used to compress gases to low pressures are finned. The fins are exposed to air which contributes to cooling of cylinder walls.

Determination of the work spent to drive the compressor. In an isothermal process the work expended to compress the gas is represented on the indicator diagram by area *01230* (Fig. 16-2). The total work to be spent to produce 1 kg of compressed gas is equal to

$l=$area *4325*+area *5216*−area *4016*.

Area $4325=p_2v_2$ represents graphically discharge work; area $4016=p_1v_1$—suction work, and area $5216=\int_{v_1}^{v_2} p\,dv$—compression work.

With isothermal compression (area *5216*) the work input is determined from Eq. (7-13); area $5216=l_{is}=p_1v_1\ln p_2/p_1$.

Allowing for the fact that at $t=\text{const}$ $p_2v_2=p_1v_1$, we find that

$$l_{is}=-p_2v_2-p_1v_1\ln\frac{p_2}{p_1}+p_1v_1=-p_1v_1\ln\frac{p_2}{p_1}. \qquad (16\text{-}4)$$

The work spent to drive the compressor is equal to the work input in isothermal compression.

The amount of heat rejected from the gas

$$q=l_{is}=-RT\ln\frac{p_2}{p_1}.$$

With reversible adiabatic compression the work input is determined from Eq. (7-16)

$$\text{area } 5'2'16=l_{ad}=\left[\frac{1}{k-1}\right](p_2v_2-p_1v_1).$$

The work spent to drive the compressor shall be equal to

$$l_{ad}^{dr} = -(p_2v_2 - p_1v_1) - \frac{1}{k-1}(p_2v_2 - p_1v_1) = -\frac{k}{k-1}(p_2v_2 - p_1v_1) =$$

$$= -\frac{k}{k-1} RT_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} - 1 \right]. \qquad (16\text{-}5)$$

The work spent to drive the compressor is k times greater than the work of adiabatic compression. Expression (16-5) can be presented in another form. The work input in adiabatic compression is equal to

$$l_{ad} = u_1 - u_2,$$

then the work spent to drive the compressor

$$l_{ad}^{dr} = -(p_2v_2 - p_1v_1) - (u_2 - u_1) = -(p_2v_2 + u_2) + (p_1v_1 + u_1) = -(i_2 - i_1). \qquad (16\text{-}6)$$

With adiabatic compression the absolute magnitude of the work spent to drive the compressor is equal to the difference between the enthalpies at the end beginning of the process of compression. This formula is true both for real and ideal gases.

For a compressor realizing polytropic compression the work input is represented by area *5″2″16*, therefore

$$l_{pol} = -(p_2v_2 - p_1v_1) - \frac{1}{n-1}(p_2v_2 - p_1v_1) = \frac{n}{n-1}(p_2v_2 - p_1v_1). \qquad (16\text{-}7)$$

The work spent to produce 1 kg of compressed gas is equal to

$$l_{pol} = -\frac{n}{n-1} RT_1 \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right]. \qquad (16\text{-}8)$$

The theoretical amount of heat rejected from the gas is determined from Eq. (7-21)

$$q = c_v \frac{n-k}{n-1}(T_2 - T_1). \qquad (16\text{-}9)$$

The real indicator diagram of a single-stage compressor (Fig. 16-3) differs from the theoretical one (Fig. 16-2) in the first place in the presence of losses due to throttling in the intake and discharge valves. In consequence, suction, or admission, takes place in the cylinder at a gas pressure less than the pressure of the surroundings from which the gas is drawn, and discharge takes place at a pressure greater than the pressure in the delivery pipeline. These losses increase with the speed (rpm) of the compressor.

In addition, in a real compressor there is a free space between the cylinder cover and the piston in its extreme discharge stroke position. This free space is referred to as the *clearance*. The clearance in the cylinder of a compressor usually amounts to from 4 to 10 per cent of the swept volume V_h (Fig. 16-3). Upon termination of the discharge of the compressed gas (line *2-3*)

some quantity of the gas remains in the cylinder clearance occupying a volume V_{cl}. During the return stroke of the piston the gas remaining in the clearance expands and the admission of a new portion of the gas shall be resumed when the gas pressure in the cylinder drops to the intake pressure or to the pressure of the surroundings from which the gas is drawn. The

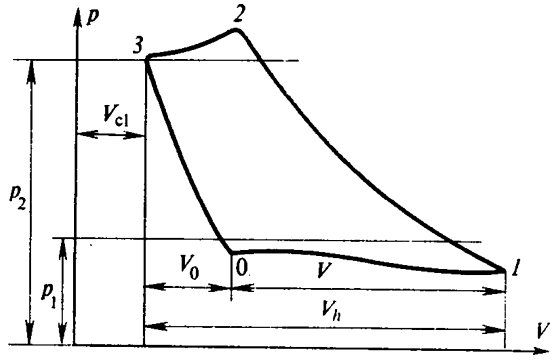


FIG. 16-3

process of expansion of the residual compressed gas in the cylinder clearance is represented by line *3-0*. Suction of gas into the compressor shall initiate only at point *0* and the volume of the fresh gas filling the cylinder shall be $V_h - V_0 = V$. The clearance decreases the quantity of the gas drawn into the cylinder, diminishing, thereby, the output of the compressor. The ratio of volume V to volume V_h is referred to as the *volumetric efficiency*

$$\eta_v = \frac{V}{V_h}.$$

The volumetric efficiency of a compressor diminishes with increasing clearance, and at a definite value of V_{cl} may become equal to zero. With a constant V_{cl} and a rise in compression pressure the volumetric efficiency and the output will also diminish, and in the limiting case, when the compression line intersects the clearance line, the volumetric efficiency becomes zero. This phenomenon is illustrated in Fig. 16-4. In the first case, when the process of compression, line *1-2*, terminates at a pressure p_2, the delivery, or discharge, is effected along line *2-3*. The cylinder pressure drops along line *3-0* and admission begins at point *0*. In the second case, with an increase

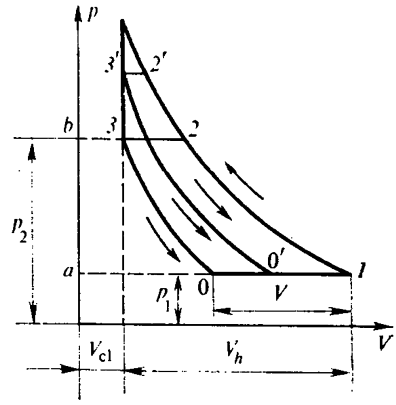


FIG. 16-4

in pressure p_2, compression ends at point *2'* and the discharge proceeds along line 2'-3'. Considerably less compressed gas is then delivered, compared to the first case. In the third case, with a further increase in pressure p_2, compression terminates at point *4*, i.e. at the spot where the compression line intersects the clearance line; in this case the discharge line turns into a point, and no admission of a fresh portion of gas into the cylinder takes place.

The piston of a performing compressor compresses periodically the same quantity of gas without any delivery. The volumetric efficiency of the compressor and the output then become equal to zero. The quantity of the gas admitted into the cylinder shall decrease still more due to the increase of the specific volume of the gas as a result of heating of the gas by the heated surfaces of the cylinder and the hot gas, remaining in the clearance. The decrease in the mass of the gas drawn into the cylinder due to an increase in gas temperature is determined by the ratio T_1'/T_1, where T_1'=the temperature of the admitted gas; T_1=the temperature of the gas heated in the cylinder during the admission stroke.

The total decrease of the output of a compressor due to the presence of a clearance and to the heating of the gas is characterized by the coefficient of admission

$$\eta_{ad}=\eta_v \frac{T_1'}{T_1}. \qquad (16\text{-}10)$$

The total theoretical work spent to drive a compressor with a cylinder clearance is represented by area *12301* in Fig. 16-4.

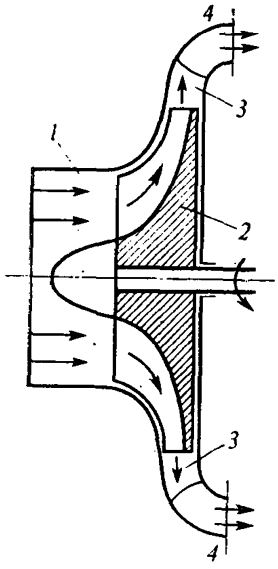


FIG. 16-5

The decrease of the output of a compressor with increasing discharge pressure makes it impossible to produce high-pressure gases in one cylinder. In addition, at high compression pressures, the temperature of the compressed gas may exceed the self-ignition temperature of the lubricating oil used in the cylinder, and that must be avoided. A single-stage compressor is usually operated to compress gases to a pressure of 6 to 10 bar.

Centrifugal blowers (turbo-compressors and axial-flow compressors) differ from reciprocating (piston) compressors by their continuous operation. Besides, the working medium in these compressors is displaced with considerable velocities. A centrifugal, or rotary, compressor consists of the following main parts (Fig. 16-5): inlet connection *1*, impeller *2*, diffuser *3* and delivery connections *4*. The handled gas passes through the inlet connection into the channels

formed between the blades of the impeller. As the impeller revolves, the gas, acted upon by centrifugal forces, is thrown into the diffuser where it is compressed as required, i.e. compression is realized due to a deceleration of gas flow.

To force the gas to flow through the compressor work l_{real} is spent and heat q_{real} is rejected (q_{real} does not contain heat due to friction, q_{fr}). If the inlet properties of the gas flow are p_1, t_1, v_1 and w_1, and the outlet properties—p_2, t_2, v_2 and w_2, then the main equation of flow acquires the following appearance

$$l_{real} = -(i_2 - i_1) - \frac{w_2^2 - w_1^2}{2} + q_{real}.$$

If the difference between the inlet and outlet kinetic energies of flow is small and can be neglected, then

$$l_{real} = -(i_2 - i_1 - q_{real}).$$

This expression coincides with the equation for piston compressors.

For a gas flow process the equation of the first law of thermodynamics has the following appearance:

$$q_{real} + g_{fr} = i_2 - i_1 - \int_{p_1}^{p_2} v\,dp.$$

Substituting the value of q_{real} into the expression for work l_{real}, we obtain the formula for the amount of work spent to drive a centrifugal compressor

$$l_{real} = -\int_{p_1}^{p_2} v\,dp - q_{fr},$$

which fully coincides with the equation for reciprocal compressors.

Processes of compression in a real compressor. The process of compression in a real compressor is characterized by the presence of internal losses due to friction and heat exchange with the surroundings. When designing compressors it is assumed that the work to be spent to drive a cooled compressor is equal to the work involved in isothermal compression, and for a non-cooled compressor—to the work spent in adiabatic compression. The effective performance of a real compressor is determined by its isothermal and adiabatic efficiencies. These efficiencies are the ratios of the theoretical work to the real work actually spent to drive the compressor

$$\eta_{is} = \frac{l_{is}}{l_{real}}; \quad \eta_{ad} = \frac{l_{ad}}{l_{real}}.$$

Let us plot on a *T-s* diagram a reversible *1-2* and (arbitrarily) an irreversible *1-3* (actual process) adiabat (Fig. 16-6). In accordance with Eq. (16-3) the

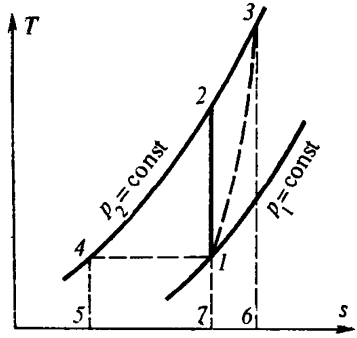


FIG. 16-6

real work l_{real} spent to drive a compressor operated on the adiabatic cycle is equal to

$$l_{ad}=-(i_3-i_1)=-c_p(T_3-T_1),$$

and the theoretical work l_t in reversible adiabatic compression

$$l_t=-c_p(T_2-T_1),$$

whence the adiabatic efficiency of a compressor is equal to

$$\eta_{ad}=\frac{T_2-T_1}{T_3-T_1} \qquad (16\text{-}11)$$

The irreversible adiabat can be considered conditionally, with a certain approximation, as some polytrope with an exponent $n>k$, the numerical value of which depends on the magnitude of the frictional forces. Then

$$\frac{T_2}{T_1}=\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}, \quad \frac{T_3}{T_1}=\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}$$

whence

$$\eta_{ad}=\frac{\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}-1}{\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}-1}. \qquad (16\text{-}12)$$

The average value of the polytropic exponent n is determined by the properties of the gas at the beginning and end of compression. The real work spent to drive a non-cooled compressor will be

$$l_{real}=\frac{l_t}{\eta_{ad}},$$

or

$$l_{real}=-\frac{k}{k-1}RT_1\left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}-1\right]. \qquad (16\text{-}13)$$

The real work spent to drive a non-cooled compressor can be determined if the conditional polytropic exponent n for real process of compression is known. On the *T-s* diagram (Fig. 16-6) the real work l_{real} is represented by area *3456*, and the theoretical work input l_t—by area *2457* (only valid for ideal gases).

For a cooled compressor it is not sufficient to know just the magnitude of the polytropic exponent n, since in the absence of heat transfer from the

compressor the same polytropic exponent may correspond to different values of the work due to friction, q_{fr}.

The effective horsepower spent to drive a compressor is determined by formula

$$N_e = \frac{l_{dr} m}{\eta_{pol} \eta_{mech} \eta_{ad}} \tag{16-14}$$

where l_{dr} = work spent to drive a compressor operated by polytropic compression of a gas, J/kg;

m = output of compressor per second, equal to $V_{st}\varrho_{st}$, where V_{st}=volumetric output of compressor under standard atmospheric conditions; ϱ_{st}=gas density under standard atmospheric conditions;

η_{pol} = compressor efficiency with polytropic gas compression;

η_{mech} = mechanical efficiency allowing for frictional losses;

η_{ad} = coefficient of admission.

16-2. Multistage Compressor

High-pressure gas is produced in multistage compressors (Fig. 16-7) which compress the gas polytropically in several series-connected cylinders, with intermediate cooling after each compression in a cylinder.

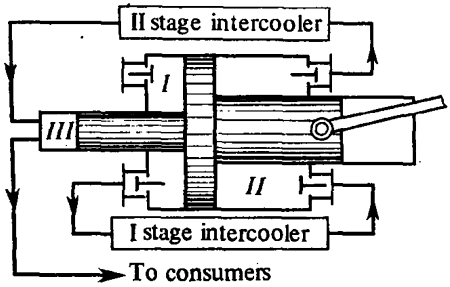


FIG. 16-7

Compression of a gas in several cylinders reduces the pressure ratio in each of the cylinders and raises the volumetric efficiency of the compressor. In addition, intercooling of the gas after each stage contributes to better lubrication of the piston in the cylinder and reduces the work spent to drive the compressor.

The ideal indicator diagram of a three-stage compressor is shown in Fig. 16-8 in which *0-1* is the suction line for the first stage; *1-2*—polytropic compression in the first stage; *2-a*—line of delivery from the first stage into the first intercooler; *a-3*—line of admission into the second stage; *3-4*—polytropic compression in the second stage; *4-6*—line of delivery from the second

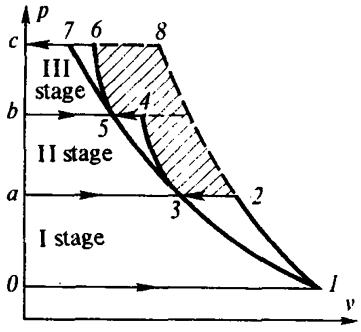


FIG. 16-8

stage into the second intercooler; *b-5*—line of suction into the third cylinder; *5-6*—polytropic compression in the third stage; *6-c*—line of delivery from the third stage into a receiver or to industrial users.

The lines *2-3* and *4-5* represent the reduction in the volume of the handled gas due to cooling at a constant pressure in the first and second intercoolers. The compressed gas is cooled in all intercoolers to the same temperature, equal to the initial temperature T_1, therefore the temperature of the gas at points *1*, *3* and *5* shall be the same and lie on the isotherm *1-7*.

Compressors are usually operated with the same pressure ratio in all cylinders

$$\frac{p_2}{p_1}=\frac{p_4}{p_3}=\frac{p_6}{p_5}=x. \tag{16-15}$$

Under the assumed conditions this pressure ratio ensures a minimum consumption of work in driving a multistage compressor*.

With the same pressure ratio in all stages, equal initial temperatures and polytropic exponents, the final temperatures in the individual stages of the compressor shall also be the same, i.e.

$$T_2=T_4=T_6.$$

It follows from Eq. (16-15) that

$$x^3=\frac{p_2p_4p_6}{p_1p_3p_5},$$

whence the degree of increase in pressure in each stage is equal to

$$x=\sqrt[3]{\frac{p_6}{p_1}},$$

or with a z number of stages we obtain

$$x=\sqrt[z]{\frac{p_z}{p_1}}. \tag{16-16}$$

The degree of increase in pressure in each stage of a multistage compressor is equal to the z root of the ratio of the final pressure p_z to the initial pressure p_1.

* No proof of the assumption is given here.

The total work input for driving a three-stage compressor by polytropic compression of the gas in each stage is represented on the indicator diagram by area *0123456cO*.

If the gas is compressed polytropically to a pressure p_6 in one stage, then the work consumed in driving the compressor is represented by area *018cO*. When passing from single-stage compression to three-stage compression with intercooling, a certain amount of work is saved, represented by area *2345682*. Multistage compression with intercooling brings the operating process of a compressor close to the most efficient isothermal process.

With equal stage inlet temperatures and the same pressure ratio in all compressor cylinders, we obtain equal amounts of work consumed in all stages of a compressor:

work input in the first stage

$$l_1=\frac{n}{n-1}p_1v_1\left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}-1\right]=\frac{n}{n-1}RT_1\left[\frac{p_2}{p_1}^{\frac{n-1}{n}}-1\right];$$

work input in the second stage

$$l_2=\frac{n}{n-1}p_3v_3\left[\left(\frac{p_4}{p_3}\right)^{\frac{n-1}{n}}-1\right]=\frac{n}{n-1}RT_3\left[\left(\frac{p_4}{p_3}\right)^{\frac{n-1}{n}}-1\right];$$

work input in the third stage

$$l_3=\frac{n}{n-1}p_5v_5\left[\left(\frac{p_6}{p_5}\right)^{\frac{n-1}{n}}-1\right]=\frac{n}{n-1}RT_5\left[\left(\frac{p_6}{p_5}\right)^{\frac{n-1}{n}}-1\right],$$

whence

$$l_1=l_2=l_3.$$

The total work, J/kg, expended to compress a gas in the three stages of a compressor is equal to

$$l_c=3l_1, \tag{16-17}$$

or for m kg of gas

$$L_c=3ml_1. \tag{16-18}$$

The work expended to drive a multistage compressor is equal to the work input of one stage multiplied by the number of stages.

With a gas being compressed under the same conditions the same quantities of heat are transferred from the gas in individual stages, in accordance with Eq. (7-24)

$$q=c_v\frac{n-k}{n-1}(t_1-t_2). \tag{16-19}$$

The quantity of heat rejected from the gas in any intercooler in which isobaric cooling of the gas is realized is found from the formula

$$q_p=c_{pm}(t_2-t_1). \tag{16-20}$$

On the *T-s* diagram shown in Fig. 16-9 processes of adiabatic compression in a three-stage compressor are represented by the straight lines *1-2*, *3-4* and *5-6*, and the processes of cooling in the intercoolers—by the curves *2-3*, *4-5* and *6-7*. The processes of polytropic compression are represented in Fig. 16-10 by the curves *1-2*, *3-4* and *5-6*, and the processes of cooling in the intercoolers—by the lines *2-3*, *4-5* and *6-7*. With the same gas temperatures at the inlets to the compressor cylinders, $T_1=T_3=T_5$, and equal gas

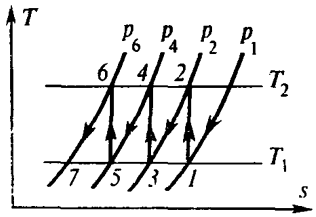


FIG. 16-9

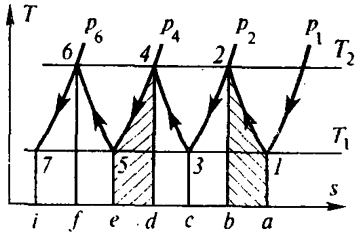


FIG. 16-10

outlet temperatures $T_2=T_4=T_6$ the areas *a12b*, *c34d* and *e56f* are equal to one another, which indicates that the same amounts of heat are removed from the compressed gas in all the cylinders. Areas *b23c*, *d45e* and *f67i* are also equal to one another, and from this it follows that with isobaric cooling equal amounts of heat are removed from the compressed gas in the intercoolers of a multistage compressor.

Typical Questions and Examples to Chapter Sixteen

1. What machine is called a compressor?
2. Give a description of a single-stage compressor.
3. Theoretical indicator diagram of a single-stage compressor.
4. What processes are possible when a gas is compressed in a compressor?
5. Which compression process is the most advantageous one and which one involves a maximum expenditure of work?
6. What equations determine the amount of work expended to drive a compressor under isothermal, adiabatic and polytropic compression of a working medium?
7. What is the difference between a real indicator diagram and a theoretical one?
8. Why is it impossible to compress a gas to a high pressure in a single-stage compressor?
9. What is meant by the clearance in a compressor cylinder?
10. Give the definition of the volumetric efficiency.
11. How does the clearance affect gas compression?
12. What compression pressures can be realized in a single-stage compressor?

13. What is a multistage compressor used for?
14. Give a description of the design of a multistage compressor.
15. What are the peculiarities of the theoretical indicator diagram of a multistage compressor?
16. Under what conditions is multistage compression realized?
17. What is the advantage of multistage compression compared with single-stage compression?
18. Determine the work expended to drive a multistage compressor.
19. Determine the amount of heat transferred (rejected) from a compressed gas in individual stages.
20. Determine the amount of heat removed from a compressed gas in intercoolers under isobaric cooling.

Example 16-1. Determine the theoretical work input for a single-stage and multistage compressor used to compress air to a pressure of 125 bar. Initial pressure is 1 bar and temperature—300 K. The polytropic exponent is assumed to be $n=1.2$ for all stages. Determine the work input per 1 m^3 of air and the temperature at the end of compression in a single-stage, three-stage and four-stage compressor.

Single-stage compressor. The work expended to drive the single-stage compressor is equal to

$$L_c=-\frac{n}{n-1}p_1v_1\left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}-1\right]=-\frac{1.2}{1.2-1}\times 1\times 10^5\left[\left(\frac{125}{1}\right)^{\frac{1.2-1}{1.2}}-1\right]=$$

$$=6\times 10^5(2.24-1)=-744 \text{ kJ/m}^3.$$

The temperature at the end of compression

$$\frac{T_2}{T_1}=\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}; \quad T_2=300\times 2.24=672 \text{ K}.$$

Three-stage compressor. The air compression ratio in each stage of the compressor is determined by Eq. (16-16)

$$x=\sqrt[z]{\frac{p_z}{p_1}}=\sqrt[3]{\frac{125}{1}}=5.$$

The work expended to produce compressed air in the first stage is equal to

$$L_1=-\frac{n}{n-1}p_1v_1\left[\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}-1\right]=-\frac{1.2}{0.2}\times 1\times 10^5(5^{0.167}-1)=-186.0 \text{ kJ/m}^3.$$

Equal amounts of work are spent in all stages, therefore the total work input to drive the compressor is equal to

$$L_c=3L_1=-186\times 3=-558 \text{ kJ/m}^3.$$

The temperature at the end of compression in each stage is

$$\left(\frac{T_2}{T_1}\right)=\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}=5^{0.167}=1.31;$$

$$T_2=T_1\times 1.31=300\times 1.31=393 \text{ K}.$$

When passing from single-stage to three-stage compression of air the work input diminishes by

$$\frac{-744-(-558)}{-744}\times 100=25.0 \text{ per cent}.$$

If air is compressed to a pressure of 125 bar in a four-stage compressor with a compression ratio $x=3.34$, then the total work input for driving the compressor shall amount to

$$L_c=488 \text{ kJ/m}^3.$$

The temperature at the end of compression in each stage

$$T_2=T_1\times 1.22=300\times 1.22=366 \text{ K}.$$

Compared with a single-stage compressor the work input shall diminish by

$$\frac{-744-(-488)}{-744}\times 100=34.4 \text{ per cent};$$

and compared with a three-stage compressor the expended work to drive the compressor shall diminish by

$$\frac{-588-(-448)}{-558}\times 100=12.5 \text{ per cent}.$$

CHAPTER SEVENTEEN

CYCLES OF INTERNAL COMBUSTION ENGINES

17-1. Brief Historical Introduction

From the analysis of a direct reversible cycle it follows that with an increase of the mean temperature of high-temperature sources and a decrease of the mean temperature of low-temperature sources the thermal efficiency of the cycle increases.

Up to the seventies of the last century the only source of mechanical work was the steam engine operated with low-temperature and low-pressure steam. The high-temperature gases resulting from fuel combustion were first directed into steam boilers to generate low-pressure steam which was used as a working medium. Such utilization of the heat of fuel resulted in low thermal efficiencies of steam power plants.

The studies and research conducted by scientists and inventors of many countries led to the creation of a new engine in which the gases resulting from fuel combustion exerted direct action on the piston of the machine. Machines of this kind, in which the fuel is fired directly in the cylinder underneath a piston are referred to as *reciprocating internal combustion engines.*

One of the first who indicated the possibility of creating an internal combustion engine was Sadi Carnot. In 1824, in his work "Réflexions sur la puissance motrice du feu et sur les machines propres á développer cette puissance" [English translation: Carnot, S. *Reflections on the Motive Power of Fire,* New York, Dover (1960)] Carnot wrote that it would seem to us preferable to compress the air by means of pumps, to make it traverse a perfectly closed furnace into which combustible substance had been introduced in small portions by a mechanism easy of conception, to make it develop its action in a cylinder with a piston, or in another variable space; finally to throw it again into the atmosphere, or even to make it pass under a steam boiler to utilize the temperature remaining. Carnot's ideas were subsequently fully realized.

In 1860, the French mechanic J. Lenoir constructed an internal combustion engine in which lighting gas was fired, but without preliminary compression of the working medium. This engine has not found wide application due to its low efficiency, not higher than that of steam engines. In 1862, the French engineer A. Beau de Rochas was granted a patent for an engine based on construction principles coinciding with the ideas suggested by Carnot. In 1877, the German engineer N. Otto constructed a petrol (gasoline) engine performing on the principle suggested earlier by A. Beau de Rochas.

In 1897, the German engineer R. Diesel elaborated a high-compression kerosene-fired engine in which kerosene was atomized in the engine cylinder by high-pressure air delivered from a compressor. Russian engineers perfected and improved to a considerable extent the Diesel engine.

The Russian engineer Mamin created in 1893 a high-compression engine in which crude oil was fired featuring airless injection and mechanical atomization of the fuel. In 1898, at the Petersbourg Nobel works, the first air-injection engine was constructed, operating on crude oil. In 1903, at the same works, the first reversible marine engine was constructed, capable of firing heavy grades of fuel. Up to the present time heavy fuel-fired engines remain the most efficient with respect to fuel consumption.

In 1904, the Russian engineer G. V. Trinkler constructed an airless-injection engine in which first constant-volume fuel combustion takes place, then combustion proceeds at a constant pressure. Such an engine with mixed, or dual fuel combustion has presently found wide application all over the world.

Thus, during a period of 40 to 50 years high-efficiency internal combustion engines were created and Russian and Soviet scientists and engineers greatly contributed to the construction and perfection of these engines.

All modern reciprocating internal combustion engines are subdivided into three groups: (1) engines featuring rapid fuel combustion at a constant volume; (2) engines with gradual fuel combustion at a constant pressure; and (3) engines with mixed (dual) fuel combustion, partly at a constant volume and partly at a constant pressure.

In investigating the ideal thermodynamic cycles of reciprocating internal combustion engines, the usual procedure is to first determine the quantity of added and rejected heat and the main parameters of state of the working medium, with the temperatures at intermediate points being calculated as functions of the initial temperature of the gas; then the thermal efficiency of the cycle is calculated by the main characteristics, and the thermal efficiency is analyzed.

The main characteristics, or parameters, of any cycle of an internal combustion engine are the following dimensionless quantities:

compression ratio

$$\varepsilon=\frac{v_1}{v_2},$$

which is the ratio of the initial specific volume of the working medium to its specific volume at the end of compression;

pressure ratio

$$\lambda=\frac{p_3}{p_2},$$

that represents the ratio of pressures at the end and beginning of the isochoric process of heat addition;

degree of preliminary expansion, or degree of isobaric expansion

$$\varrho = \frac{v_3}{v_2},$$

representing the ratio of the volumes at the end and beginning of the isobaric process of heat addition.

17-2. Cycle with Heat Addition at v = const

It is expedient to investigate the cycle of a real reciprocating internal combustion engine on a diagram presenting the change of cylinder pressure as a function of piston position during the entire cycle. Such a diagram, made with the aid of a special instrument, an indicator, is called an *indicator diagram.* The area of the plane figure drawn on the indicator diagram represents the indicated work done by the gas per cycle according to a certain scale factor.

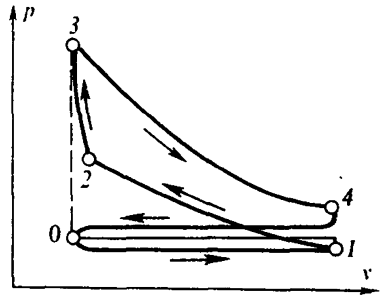


FIG. 17-1

Shown in Fig. 17-1 is the indicator diagram of an internal combustion engine realizing rapid fuel combustion at a constant volume. The combustible substance used to operate such engines is usually light fuel, such as gasoline, town or producer gas, alcohols, etc.

During the piston stroke from the left dead position to the extreme left position the combustible mixture consisting of vapours and fine particles of fuel and air is drawn through the inlet, or admission valve. On the indicator diagram this process is depicted by the curve *0-1* which is called the *admission curve.* It is clear that the line *0-1* does not represent a thermodynamic process since the main parameters do not change along it, and only the mass and volume of the mixture in the cylinder change. During the return stroke of the piston the inlet valve closes and compression of the combustible mixture takes place. The process of compression is represented on the indicator diagram by the curve *1-2*, called the *compression line.* At point *2*, when the piston has come close to but not yet reached the left dead point, the combustible mixture is ignited by an electric spark. The combustion of the fuel-air mixture is almost instantaneous, i.e. practically at a constant volume. This process is represented on the indicator diagram by curve *2-3.* Fuel combustion results in an abrupt increase of gas temperature and a rise in pressure (point *3*). Then the products of combustion expand. The piston travels to the right dead point and the gases perform useful work. On the indicator diagram the process of expansion is represented by curve *3-4*, referred to as the *expansion line.* At point *4* the exhaust valve opens and cylinder pressure drops almost to external pressure. During the further travel of the piston from right to left the products of combustion

are discharged from the cylinder through the exhaust valve at a pressure somewhat above atmospheric pressure. This process is represented on the indicator diagram by curve *4-0*, referred to as the *exhaust line.*

The operating process considered is realized during four strokes of the piston or two revolutions of the shaft. Such internal combustion machines are called *four-stroke engines.*

It is clear from the description of the performance of a real internal combustion engine with rapid fuel combustion at a constant volume that the operating process is not a closed one. It includes all symptoms of irreversible processes: friction, chemical reactions in the working medium, finite piston velocities, heat exchange at a finite temperature difference and so on.

It is impossible to analyze such a cycle from the viewpoint of the theory of heat processes, that is why thermodynamics investigates not real processes of internal combustion engines, but ideal reversible cycles. The working medium is assumed to be an ideal gas with a constant heat capacity. The cylinder is filled with a constant amount of the working medium. The difference between the temperatures of the heat source and the working medium is infinitely small. Heat is added to the working medium from external heat sources, and not at the expense of fuel combustion, and the same must be said concerning the rejection (removal) of heat.

Thus, a study of ideal thermodynamic cycles makes it possible to observe the assumptions made, to analyze and compare the performance of different engines and to identify the factors affecting their efficiency. The diagram plotted on the assumed conditions is not the indicator diagram of an internal combustion engine, but the *p-v* diagram of a cycle with heat addition at constant volume.

Let us consider the ideal thermodynamic cycle of an engine operated with isochoric (constant-volume) heat addition, consisting of two isochors and two adiabats.

The cycle plotted on the *p-v* and *T-s* diagrams, shown in Figs. 17-2 and 17-3, is realized in the following way.

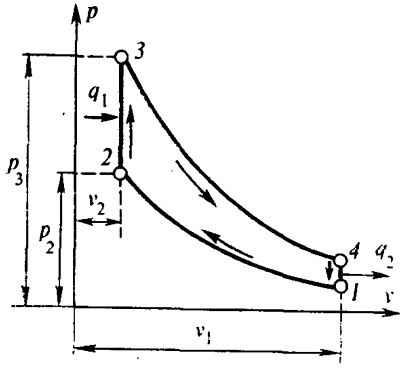


FIG. 17-2

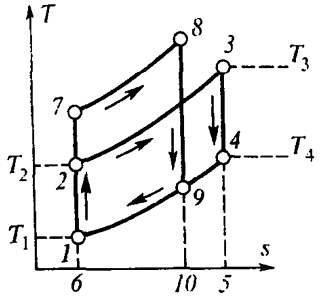


FIG. 17-3

An ideal gas with initial parameters p_1, v_1 and T_1 is compressed along adiabat *1-2* to point *2*. Along the isochor *2-3* a quantity of heat q_1 is added to the working medium. From point *3* the working medium expands adiabatically (line *3-4*), then, finally, the working medium returns along isochor *4-1* into its initial state, with heat q_2 being rejected from it into a low-temperature source.

The characteristics of the cycle are: the compression ratio $\varepsilon=v_1/v_2$ and the pressure ratio $\lambda=p_3/p_2$.

Determine the thermal efficiency of the cycle, assuming the heat capacity c_v and the quantity k to be constant.

The thermal efficiency of the cycle

$$\eta_t=\frac{q_1-q_2}{q_1}=1-\frac{q_2}{q_1}.$$

The amount of added heat

$$q_1=c_v(T_3-T_2),$$

and the quantity of rejected heat

$$q_2=c_v(T_4-T_1).$$

Then the thermal efficiency of the cycle is

$$\eta_t=1-\frac{q_2}{q_1}=1-\frac{c_v(T_4-T_1)}{c_v(T_3-T_2)}=1-\frac{T_4-T_1}{T_3-T_2}.$$

At all characteristic points of the cycles the properties of the working medium are as follows:

at point 2

$$v_2=\frac{v_1}{\varepsilon};\quad p_2=p_1\left(\frac{v_1}{v_2}\right)^k=p_1\varepsilon^k;$$

$$\frac{T_2}{T_1}=\left(\frac{v_1}{v_2}\right)^{k-1}=\varepsilon^{k-1}\quad\text{and}\quad T_2=T_1\varepsilon^{k-1};$$

at point 3

$$v_3=v_2=\frac{v_1}{\varepsilon};\quad p_3=p_2\lambda=p_1\varepsilon^k\lambda;$$

$$\frac{T_3}{T_2}=\frac{p_3}{p_2}=\lambda\quad\text{and}\quad T_3=T_2\lambda=T_1\varepsilon^{k-1}\lambda;$$

at point 4

$$v_4=v_1;\quad p_4=p_3\left(\frac{v_3}{v_4}\right)^k=p_3\left(\frac{v_3}{v_1}\right)^k=\frac{p_3}{\varepsilon^k}=p_1\lambda,$$

$$\frac{T_4}{T_3}=\left(\frac{v_3}{v_4}\right)^{k-1}=\left(\frac{v_3}{v_1}\right)^{k-1}=\frac{1}{\varepsilon^{k-1}}\quad\text{and}\quad T_4=T_1\varepsilon^{k-1}\times\lambda\frac{1}{\varepsilon^{k-1}}=T_1\lambda.$$

Substituting the found temperatures into the equation of thermal efficiency of the cycle, we obtain

$$\eta_t = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1\lambda - T_1}{T_1\varepsilon^{k-1}\lambda - T_1\varepsilon^{k-1}} = 1 - \frac{1}{\varepsilon^{k-1}}.$$

The thermal efficiency of a cycle with heat addition at a constant volume (v=const) is equal to

$$\eta_t = 1 - \frac{1}{\varepsilon^{k-1}}. \qquad (17\text{-}1)$$

It follows from Eq. (17-1) that the thermal efficiency of such a cycle depends on the compression ratio ε and the adiabatic exponent k, or on the nature of the working medium. The efficiency rises with increasing ε and k. The thermal efficiency does not depend on the pressure ratio λ.

Table 17-1 contains the thermal efficiencies of cycles with isochoric addition of heat realized with different values of ε and k.

TABLE 17-1

ε	η_t	
	at k=1.35	at k=1.4
3	32.0	36.0
4	38.0	43.0
5	42.5	47.5
6	46.5	51.5
7	49.4	55.0
8	51.7	57.0
10	55.2	61.5

On the *T-s* diagram shown in Fig. 17-3 the efficiency is determined from the ratio of areas

$$\eta_t = \frac{q_1 - q_2}{q_1} = \frac{\text{area } 6235 - \text{area } 6145}{\text{area } 6235} = \frac{\text{area } 1234}{\text{area } 6235}.$$

The dependence of thermal efficiency on the rising compression ratio ε can be vividly illustrated on the *T-s* diagram (Fig. 17-3).

With the same areas representing the added heat in two cycles, area *67810*=area *6235*, but at different compression ratios the thermal efficiency of the cycle with a greater pressure ratio, shall be higher, since a smaller quantity of heat is removed into the low-temperature source, i.e. area *61910*<area *6145*.

However an increase of the compression ratio is restricted by the possibility of untimely ignition of the combustible mixture, disturbing the normal performance of an engine. In addition, with high compression ratios the rate of fuel combustion increases abruptly which may cause detonation or

knocking (explosive combustion) that drastically decreases engine efficiency and may cause failure of engine parts. That is why for each fuel there should be practised a definite optimal compression ratio. Depending on the kind of fuel fired, the compression ratio of the engines under investigation varies from 4 to 9.

Thus, investigations indicate that internal combustion engines with the addition of heat at constant volume should never be operated with high compression ratios. In this connection the engines considered have comparatively low efficiencies.

The theoretical useful work performed by 1 kg of the working medium depends on the mutual arrangement of the processes of expansion and compression of the working medium. An increase of the average pressure difference between the expansion and compression lines makes it possible to diminish the size of the engine cylinder. If we denote the average pressure by p_1, the theoretical useful work done by 1 kg of the working medium shall amount to

$$l' = l_{exp} - l_{comp} = p_i(v_1 - v_2).$$

The quantity p_i is referred to as the *mean indicator pressure* (or the mean cycle pressure), i.e. it is a fictitious constant pressure under the action of which the piston performs in the course of one stroke work equal to the work of the entire theoretical cycle.

For the cycle realized with heat addition at $v = \text{const}$, the mean indicator pressure is determined by the formula

$$p_i = \frac{l'}{v_1 - v_2} = p_1(\varepsilon^k - \varepsilon)\frac{\lambda - 1}{k - 1}(\varepsilon - 1).$$

It follows from the above formula that p_i increases with the compression ratio ε, the pressure ratio λ and also with p_1.

On the other hand, the theoretical useful work l' done by 1 kg of the working medium per cycle is equal to the difference between the work of expansion and work of compression

$$l' = l_{exp} - l_{comp} = \frac{1}{k-1}(p_3v_3 - p_4v_4) - \frac{1}{k-1}(p_2v_2 - p_1v_1).$$

17-3. Cycle with Heat Addition at p = const

A study of cycles with heat addition at a constant volume brings to the conclusion that to raise the efficiency of an engine operated on that cycle, it is necessary to practise high compression ratios. But an increase of the compression ratio is restricted by the self-ignition, or autoignition, temperature of the fuel-air mixture. But if the air and fuel are separately compressed, this restriction becomes immaterial. When compressed to a high pressure the temperature of the air is so high that the fuel injected into the cylinder ignites without the need of any special ignition devices. Finally, separate

compression of the air and fuel makes it possible to use any cheap heavy liquid fuel, petroleum, fuel oil, resins, or coal-tar oils.

These are the great advantages of engines realizing gradual fuel combustion at a constant pressure. In engines of this kind air is compressed in the engine cylinder and the liquid fuel is atomized by compressed air delivered from a compressor. Separate compression permits application of high compression ratios (up to $\varepsilon=20$) and precludes untimely self-ignition of fuel. The process of fuel combustion at a constant pressure is ensured by corresponding adjustment of the fuel injector. The creation of such an engine is associated with the name of the German engineer Rudolf Diesel who was the first to elaborate the design of an air-injection engine.

Let us investigate the ideal cycle of an engine with gradual fuel combustion at a constant pressure, i.e. the cycle with heat addition at a constant pressure, $p=\text{const}$. This cycle is represented on p-v and T-s diagrams in Figs. 17-4 and 17-5. The cycle is realized in the following manner. The gaseous working medium with initial parameters p_1, v_1, T_1 is compressed along adiabat *1-2*; then heat q_1 is added to the working medium along the isobar *2-3*. From point *3* the working medium expands adiabatically along the line *3-4*. And,

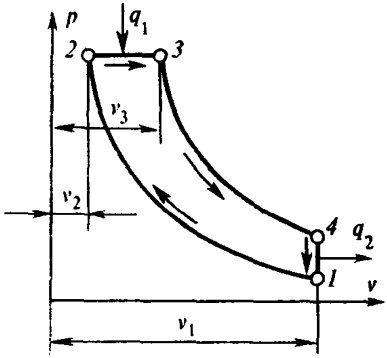


FIG. 17-4

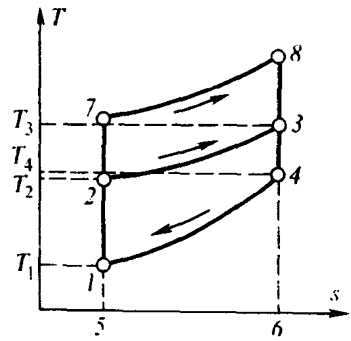


FIG. 17-5

finally, the working medium returns along the isochor *4-1* into its initial state, with heat q_2 being rejected into a low-temperature source.

The characteristics of the cycle are: the compression ratio $\varepsilon=\frac{v_1}{v_2}$ and the degree of preliminary expansion $\varrho=\frac{v_3}{v_2}$.

Let us determine the thermal efficiency of the cycle assuming the heat capacities c_v and c_p and their ratio $k=\frac{c_p}{c_v}$ to be constant.

The thermal efficiency of the cycle is equal to

$$\eta_t=\frac{q_1-q_2}{q_1}=1-\frac{q_2}{q_1}.$$

The quantity of heat added in the cycle is

$$q_1 = c_p(T_3 - T_2),$$

and the amount of rejected heat is equal to

$$q_2 = c_v(T_4 - T_1).$$

The thermal efficiency of the cycle

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{c_v(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)}.$$

At all characteristic points the parameters of the working medium are equal to:

at point 2

$$v_2 = \frac{v_1}{\varepsilon}; \quad p_2 = p_1\varepsilon^k;$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} = \varepsilon^{k-1} \quad \text{and} \quad T_2 = T_1\varepsilon^{k-1};$$

at point 3

$$v_3 = v_2\varrho = v_1\left(\frac{\varrho}{\varepsilon}\right); \quad p_3 = p_2 = p_1\varepsilon^k;$$

$$\frac{T_3}{T_2} = \frac{v_3}{v_2} = \varrho \quad \text{and} \quad T_3 = T_2\varrho = T_1\varepsilon^{k-1}\varrho;$$

at point 4

$$v_4 = v_1; \quad p_4 = p_3\left(\frac{v_3}{v_4}\right)^k = p_1\varepsilon^k\left(\frac{v_2\varrho}{v_1}\right)^k = p_1\varrho^k;$$

$$\frac{T_4}{T_3} = \left(\frac{v_3}{v_4}\right)^{k-1} = \left(\frac{v_3}{v_1}\right)^{k-1}, \quad \text{but} \quad \frac{\varrho}{\varepsilon} = \frac{v_1}{v_2} : \frac{v_3}{v_2} = \frac{v_3}{v_1},$$

or

$$T_4 = T_3\left(\frac{\varrho}{\varepsilon}\right)^{k-1} = T_1\varepsilon^{k-1}\varrho\left(\frac{\varrho^{k-1}}{\varepsilon^{k-1}}\right) = T_1\varrho^k.$$

Substituting the values of the temperatures into the equation of thermal efficiency of the cycle, we obtain

$$\eta_t = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)} = 1 - \frac{T\varrho^k - T_1}{k(T_1\varepsilon^{k-1}\varrho - T_1\varepsilon^{k-1})} = 1 - \frac{\varrho^k - 1}{k\varepsilon^{k-1}(\varrho - 1)}. \qquad (17\text{-}2)$$

It follows from Eq. (17-2) that the thermal efficiency of the cycle depends on the compression ratio ε, the exponent k and the degree of preliminary expansion ϱ. With increasing ε and k the efficiency rises and with increasing ϱ the efficiency diminishes.

Table 17-2 contains values of the thermal efficiency of a cycle realized with isobaric addition of heat at different values of ε and ϱ and the exponent $k = 1.35$.

TABLE 17-2

ε	η_t at $\varrho=1.5$	η_t at $\varrho=2.5$	p_2, bar	T_2, deg
10	52.0	46.0	—	—
12	54.0	49.0	25.7	907
14	57.0	52.0	31.8	956
16	59.0	54.0	41.4	1020
18	61.9	56.7	—	—
20	63.0	56.0	—	—

Note. p_2 and T_2 are pressure and temperature at point *2*. These quantities indicate what the temperature shall be at the end of compression process along line *1-2* and why self-ignition, or autoignition, of the fuel takes place.

On the *T-s* diagram the thermal efficiency is determined from the ratio of areas (as illustrated in Fig. 17-5)

$$\eta_t=\frac{\text{area } 5236-\text{area } 5146}{\text{area } 5236}=\frac{\text{area } 1234}{\text{area } 5236}.$$

The effect of the compression ratio on cycle efficiency is illustrated clearly on the *T-s* diagram. With equal areas representing the heat rejected into a low-temperature source (area *1456*), the efficiency of a cycle with a greater compression ratio shall be higher, since the area representing the useful work of the cycle will be greater, i.e. area *1784*>area *1234*.

The mean indicator pressure in the cycle with heat addition at $p=\text{const}$ is determined from the formula

$$p_i=\frac{l'_i}{v_1-v_2}=\frac{p_1\varepsilon}{(k-1)(\varepsilon-1)}[k\varepsilon^{k-1}(\varrho-1)-(\varrho^k-1)].$$

The mean indicator pressure increases with ε and ϱ.

The theoretical useful work l' performed by 1 kg of the working medium during one cycle is equal to the difference between the work of expansion and work due to compression

$$l'=l_{exp}-l_{comp}=p_2(v_3-v_2)+\frac{1}{k-1}(p_3v_3-p_4v_4)-\frac{1}{k-1}(p_2v_2-p_1v_1).$$

17-4. Cycle with Heat Addition at v = const and p = const or Mixed (Dual) Combustion (Heat Addition) Cycle

Internal combustion engines with gradual fuel combustion at $p=\text{const}$ possess certain demerits. One of them is the presence of a compressor for fuel injection; the power consumed to drive this compressor amounts to from 6 to 10 per cent of the total power developed by the engine. This complicates the design of the engine and reduces its efficiency. In addition, a pump and fuel injectors of intricate design must be available, etc. The power plant has a great weight.

The attempts to simplify and improve the performance of such engines have led to the creation of airless-injection engines in which the fuel is atomized by mechanical means at pressures ranging from 500 to 700 bar. The project of an airless-injection high-compression engine with dual heat addition (or dual fuel combustion) has been elaborated by the Russian engineer G. V. Trinkler. This engine is free of the shortcomings characteristic of the two types of internal combustion engines investigated above. Liquid fuel is delivered by a fuel injection pump via a fuel injector in the cylinder head as very fine droplets. Being injected into hot air, the fuel ignites and combustion of the fuel takes place continuously for the whole period that the fuel injector is open: first at a constant volume, then—at a constant pressure*.

The ideal cycle of a dual combustion engine is represented on the p-v and T-s diagrams, shown in Figs. 17-6 and 17-7. The working medium with parameters of state p_1, v_1, T_1 is compressed along adiabat *1-2* to point *2*. Then the first fraction of heat q_1' is transferred (added) to the working medium along the isochor *2-3*. The second fraction of heat q_1'' is added along the isobar *3-4*. From point *4* the working medium expands adiabatically along line *4-5*. And, finally, the working medium returns into its initial

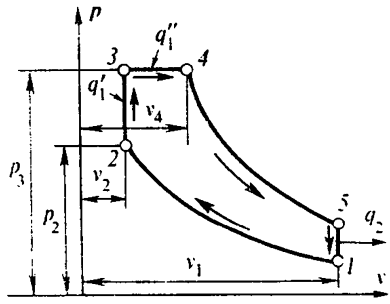


FIG. 17-6

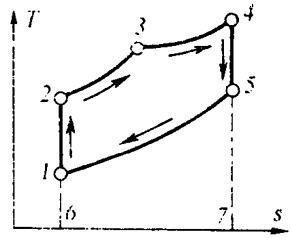


FIG. 17-7

state, point *1*, along isochor *5-1*, with an amount of heat q_2 being rejected into a low-temperature source. The characteristics of the cycle are as follows: compression ratio $\varepsilon=v_1/v_2$, pressure ratio $\lambda=p_3/p_2$ and the degree of preliminary expansion $\varrho=v_4/v_3$.

Let us determine the thermal efficiency of the dual combustion cycle on condition that the heat capacities c_p, c_v and the adiabatic exponent $k=c_p/c_v$ are constant.

* In engines of some types the fuel is atomized in a special forechamber that is usually located in the top part of the cylinder and is open to the working chamber of the cylinder through one or several narrow channels. While air is being compressed cylinder pressure increases at a rate greater than in the forechamber; due to the difference in pressures air begins to flow from the cylinder into the forechamber and this air is used to atomize the liquid fuel delivered into the forechamber.

The thermal efficiency of the cycle is

$$\eta_t=\frac{q_1-q_2}{q_1}=1-\frac{q_2}{q_1'+q_1''}.$$

The first fraction of heat added in the cycle amounts to

$q_1'=c_v(T_3-T_2)$.

The second fraction of added heat is equal to

$q_1''=c_p(T_4-T_3)$.

The quantity of heat rejected into the low-temperature source

$q_2=c_v(T_5-T_1)$.

The thermal efficiency is equal to

$$\eta_t=1-\frac{q_2}{q_1'+q_1''}=1-\frac{c_v(T_5-T_1)}{c_v(T_3-T_2)+c_p(T_4-T_3)}=1-\frac{T_5-T_1}{(T_3-T_2)+k(T_4-T_3)}.$$

At all characteristic points the parameters of the working medium are:

at point *2*

$$v_2=\frac{v_1}{\varepsilon};\quad p_2=p_1\varepsilon^k;\quad \frac{T_2}{T_1}=\left(\frac{v_1}{v_2}\right)^{k-1}=\varepsilon^{k-1}\quad\text{and}\quad T_2=T_1\varepsilon^{k-1};$$

at point *3*

$$v_3=v_2=\frac{v_1}{\varepsilon};\quad p_3=p_2=p_1\varepsilon^k\lambda;$$

$$\frac{T_3}{T_2}=\frac{p_3}{p_2}=\lambda,\quad T_3=T_2\lambda\quad\text{and}\quad T_3=T_1\varepsilon^{k-1}\lambda;$$

at point *4*

$$v_4=v_3\varrho=\frac{v_1\varrho}{\varepsilon};\quad p_4=p_3=p_1\varepsilon^k\lambda;$$

$$\frac{T_4}{T_3}=\frac{v_4}{v_3}=\varrho;\quad T_4=T_3\varrho\quad\text{and}\quad T_4=T_1\varepsilon^{k-1}\lambda\varrho;$$

at point *5*

$$v_5=v_1;\quad p_5=p_4\left(\frac{v_4}{v_5}\right)^k=p_1\varepsilon^k\lambda\left(\frac{v_1\varrho}{v_1\varepsilon}\right)^k=p_1\varrho^k\lambda;$$

$$\frac{T_5}{T_4}=\left(\frac{v_4}{v_5}\right)^{k-1}=\left(\frac{v_4}{v_1}\right)^{k-1};$$

$$\varrho:\varepsilon=\left(\frac{v_4}{v_3}\right):\left(\frac{v_1}{v_2}\right)=\frac{v_4}{v_1};$$

$$\frac{T_5}{T_4}=\left(\frac{\varrho}{\varepsilon}\right)^{k-1};\quad T_5=T_1\varepsilon^{k-1}\lambda\varrho\frac{\varrho^{k-1}}{\varepsilon^{k-1}};$$

$$T_5=T_1\lambda\varrho^k.$$

Substituting the obtained values of the temperatures at all typical, characteristic, points into the expression for the thermal efficiency of the cycle, we obtain

$$\eta_t = 1 - \frac{T_5 - T_1}{(T_3 - T_2) + k(T_4 - T_3)} = 1 - \frac{T_1 \lambda \varrho^k - T_1}{(T_1 \varepsilon^{k-1} \lambda - T_1 \varepsilon^{k-1}) + k(T_1 \varepsilon^{k-1} \lambda \varrho - T_1 \varepsilon^{k-1} \lambda)}$$

or

$$\eta_t = 1 - \frac{\lambda \varrho^k - 1}{\varepsilon^{k-1}[(\lambda - 1) + k\lambda(\varrho - 1)]} \tag{17-3}$$

It follows from Eq. (17-3) that the efficiency of the cycle depends on the exponent k, on the compression ratio, pressure ratio and degree of preliminary expansion. An increase of k, ε and λ yields a higher cycle efficiency and the efficiency diminishes with increasing ϱ.

On the T-s diagram the efficiency of the dual combustion cycle (mixed heat addition) is determined from the ratio of areas (Fig. 17-7)

$$\eta_t = \frac{\text{area } 6247 - \text{area } 6157}{\text{area } 6247_{\text{a}}} = \frac{\text{area } 12345}{\text{area } 6247}.$$

For dual combustion engines it is common practice to assume $\varepsilon = 10$ to 14, $\lambda = 1.2$ to 1.7 and $\varrho = 1.1$ to 1.5. The cycle with dual heat addition generalizes, or correlates, the two investigated cycles and Eq. (17-3) can be used to calculate the efficiency of cycles realized with isochoric (v=const) and isobaric (p=const) heat addition.

Should we assume that $\lambda = 1$ the dual combustion cycle becomes the cycle with isobaric heat addition and Eq. (17-3) reduces into the efficiency equation for this cycle, Eq. (17-2). If we assume that $\varrho = 1$, then the dual combustion cycle becomes a cycle with isochoric, or constant volume, heat addition and Eq. (17-3) reduces to the equation of thermal efficiency of this cycle, Eq. (17-1).

The theoretical useful work l' performed by 1 kg of the working medium per one cycle is equal to the difference between the work of expansion and the work of compression:

$$l' = l_{exp} - l_{comb} = p_3(v_4 - v_3) + \frac{1}{k-1}(p_4 v_4 - p_5 v_5) - \frac{1}{k-1}(p_2 v_2 - p_1 v_1).$$

The mean indicator pressure in a dual combustion cycle is

$$p_i = \frac{l'}{v_1 - v_2} = \frac{p_1}{(\varepsilon - 1)(k-1)} + \frac{1}{k-1} \times (p_4 v_4 - p_5 v_5) - \frac{1}{k-1}(p_2 v_2 - p_1 v_1).$$

17-5. Comparison of Cycles of Reciprocating Internal Combustion Engines

The degree of perfection of any cycle is determined by the magnitude of its thermal efficiency. Cycles are usually compared on the T-s diagram with the aid of two methods: the first method consists in comparing the areas on the T-s diagram, and the second method involves a comparison of the

integral mean temperatures at which heat is added and rejected in the cycles compared.

Comparison of cycles with isochoric and isobaric heat addition realized with different compression ratios, the same quantities of rejected heat and the same maximum cycle temperatures T_3. In Fig. 17-8 the cycle with isochoric heat addition is represented by the area *1234* and the cycle with isobaric, or constant-pressure, heat addition—by area *1534;* the maximum temperatures of the two cycles at point *3* are the same. The quantity of heat rejected in the two cycles is represented by the area *6147*. Since the heat added in the constant-pressure cycle is represented by an area greater than that representing the amount of heat added in the constant-volume cycle, i.e. since area *6537* > area *6237*, the efficiency of the cycle with isobaric heat addition is greater than the efficiency of the cycle realized with $v=\text{const}$.

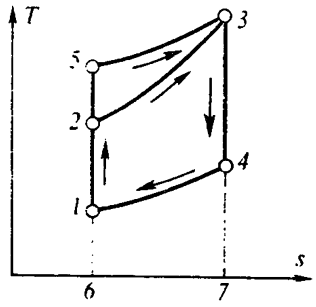


FIG. 17-8

Comparison of cycles with isochoric and isobaric heat addition by the method of integral mean temperatures. As was stated above (Sec. 8-16), the thermal efficiency of all cycles is determined by the same equation (8-31), according to which

$$\eta_t = 1 - \frac{T_{2im}}{T_{1im}},$$

where T_{1im} = integral mean temperature at which heat is added;
T_{2im} = integral mean temperature at which heat is rejected.

When comparing cycles realized with different compression ratios (Fig. 17-8) we find out that the temperature T_{1im} of isobaric heat addition is higher than the temperature T_{1im} at which heat is added isochorically and the temperature T_{2im} of isochoric heat rejection is the same for the two cycles. From this it follows that

$$\eta_{t\,isobar} > \eta_{t\,isochor}.$$

Typical Questions and Examples to Chapter Seventeen

1. Into what groups are classified reciprocating internal combustion engines?
2. Give the definitions of the main characteristics of cycles.
3. Give a description of the indicator diagram of an internal combustion engine realizing rapid fuel combustion at a constant volume.
4. Give a description of the ideal thermodynamic cycle with constant-volume heat addition, derive the calculation formula for the thermal efficiency and analyze the thermal efficiency.

5. How is the working process in an internal combustion engine with rapid fuel combustion at a constant pressure realized? What kind of fuel is fired, why is it impossible to practise high compression ratios in engines of this type?

6. Give a description of the cycle of an internal combustion engine with heat addition at $p=\text{const}$ and compare the cycle with that in which heat is added to the working medium at $v=\text{const}$.

7. How is the working process in an internal combustion engine with gradual fuel combustion at $p=\text{const}$ realized and what fuel injection methods are applied?

8. Describe the ideal cycle of an internal combustion engine operated with heat addition at $p=\text{const}$ and derive the formula of the thermal efficiency. Depict the cycle on the *T-s* diagram and make an analysis of the thermal efficiency of the cycle.

9. What were the reasons for the creation of internal combustion engines with dual, or mixed, fuel combustion?

10. Give a description of the ideal cycle of an internal combustion engine realizing mixed, or dual, fuel combustion, derive the formula of the thermal efficiency, plot the cycle on the *T-s* diagram and analyze the cycle.

11. Compare the cycles in which heat is added to the working medium at $v=\text{const}$ and $p=\text{const}$, realized with different compression ratios and the same maximum cycle temperatures, making use of the area-comparison method and the method of integral mean temperatures.

Example 17-1. For an ideal cycle of a reciprocating internal combustion engine in which heat is added to the working medium at $v=\text{const}$ determine the parameters at all main points, the useful work, find the amounts of added and rejected heat, the thermal efficiency of the Carnot cycle realized in problem conditions, the thermal efficiency of the cycle and the mean indicator pressure (Fig. 17-2) if the following conditions are given: $p_1=1$ bar, $T=320$ K, compression ratio $\varepsilon=4.0$, pressure ratio $\lambda=4.0$. The working medium is air whose gas constant $R=287$ J/kg·deg, the adiabatic exponent $k=1.4$. The heat capacity of the working medium is assumed to be constant. Carry out the calculations for 1 kg of the working medium. The parameters at point *1:*

$$p_1=1 \text{ bar}; \quad T_1=320 \text{ K};$$

$$v_1=\frac{RT_1}{p_1}=\frac{287\times 320}{10^5}=0.92 \text{ m}^3/\text{kg};$$

Parameters at point *2:*

$$v_2=\frac{v_1}{\varepsilon}=\frac{0.92}{4.0}=0.23 \text{ m}^3/\text{kg};$$

$$\frac{p_2}{p_1}=\left(\frac{v_1}{v_2}\right)^k=\varepsilon^k; \quad p_2=p_1\varepsilon^k=1\times 4^{1.4}=7.38 \text{ bar};$$

$$T_2=\frac{p_2v_2}{R}=\frac{7.38\times 0.23\times 10^5}{287}=592 \text{ K}.$$

Parameters at point *3:*

$v_3=v_2=0.23$ m³/kg; $p_3=p_2\lambda=7.38\times4=29.6$ bar;

$T_3=T_2\lambda=592\times4=2368$ K.

Parameters at point *4:*

$v_4=v_1=0.92$ m³/kg;

$$\frac{T_4}{T_3}=\left(\frac{v_3}{v_4}\right)^{k-1}=\left(\frac{v_2}{v_1}\right)^{k-1}=\frac{1}{\varepsilon^{k-1}};$$

$$T_4=\frac{T_3}{\varepsilon^{k-1}}=\frac{2368}{4^{0.4}}=1340 \text{ K};$$

$$p_4=\frac{RT_4}{v_4}=\frac{287\times1340}{0.92\times10^5}=4.17 \text{ bar}.$$

The work of expansion is equal to

$$l_1=\frac{1}{k-1}(p_3v_3-p_4v_4)=\frac{10^5}{0.4}(29.6\times0.23-4.17\times0.92)=$$

$$=742\,000 \text{ J/kg}=742 \text{ kJ/kg}.$$

The work of compression

$$l_2=\frac{1}{k-1}(p_1v_1-p_2v_2)=\frac{10^5}{0.4}(1\times0.92-7.38\times0.23)=$$

$$=-195\,000 \text{ J/kg}=-195 \text{ kJ/kg}.$$

The useful work is determined as

$l=l_1+l_2=742-195=547$ kJ/kg.

The quantity of heat added

$$q_1=c_v(T_3-T_2)=\frac{20.78}{28.85}(2368-592)=1280 \text{ kJ/kg}.$$

The quantity of heat rejected

$$q_2=c_v(T_4-T_1)=\frac{20.78}{28.85}(1340-320)=737 \text{ kJ/kg}.$$

The amount of usefully employed heat is equal to

$q=1280-737=543$ kJ/kg.

The thermal efficiency of the cycle is

$$\eta_t=\frac{q}{q_1}=\frac{543}{1280}=0.425.$$

Checking the thermal efficiency of the cycle

$$\eta_t=1-\frac{1}{\varepsilon^{k-1}}=1-\frac{1}{4^{0.4}}=0.426.$$

By the conditions of the problem the thermal efficiency of the Carnot cycle is equal to

$$\eta_t = 1 - \frac{T_1}{T_3} = 1 - \frac{320}{2368} = 0.865.$$

The mean indicator pressure is equal to

$$p_i = \frac{l}{v_1 - v_2} = \frac{547\,000}{(0.92 - 0.23) \times 10^5} = 7.9 \text{ bar.}$$

Example 17-2. For an ideal reciprocating combustion engine operated with heat addition at $p = \text{const}$ determine the parameters at all main points, the useful work, quantities of added and rejected heat, find the thermal efficiency of the Carnot cycle for the given conditions, the mean indicator pressure (see Fig. 17-4) assuming $p_1 = 1$ bar, $T_1 = 350$ K, compression ratio $\varepsilon = 20$, the degree of isobaric expansion $\varrho = 2$; the working medium is air with a gas constant $R = 287$ J/kg·deg, the adiabatic exponent $k = 1.4$. The heat capacity of the working medium is assumed to be constant. Carry out calculations for 1 kg of the working medium.

Parameters at point *1:*

$$p_1 = 1 \text{ bar}; \quad T_1 = 350 \text{ K}; \quad v_1 = \frac{RT_1}{p_1} = \frac{287 \times 350}{10^5} = 1.0 \text{ m}^3/\text{kg}.$$

Parameters at point *2:*

$$v_2 = \frac{v_1}{\varepsilon} = \frac{1}{20} = 0.05 \text{ m}^3/\text{kg};$$

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^k = \varepsilon^k; \quad p_2 = p_1 \varepsilon^k = 1 \times 20^{1.4} = 66.2 \text{ bar};$$

$$T_2 = \frac{p_2 v_2}{R} = \frac{66.2 \times 0.05 \times 10^5}{287} = 1155 \text{ K}.$$

Parameters at point *3:*

$$\frac{v_3}{v_2} = \frac{T_3}{T_2} = \varrho, \quad T_3 = T_2 \varrho = 1155 \times 2 = 2310 \text{ K};$$

$$p_3 = 66.2 \text{ bar}; \quad v_3 = v_2 \varrho = 0.05 \times 2 = 0.1 \text{ m}^3/\text{kg}.$$

Parameters at point *4:*

$$v_4 = 1.0 \text{ m}^3/\text{kg}$$

$$\frac{T_4}{T_3} = \left(\frac{v_3}{v_4}\right)^{k-1}; \quad T_4 = 2310 \times 0.1^{0.4} = 920 \text{ K};$$

$$p_4 = \frac{RT_4}{v_4} = \frac{287 \times 920}{10^5} = 2.64 \text{ bar}.$$

The work of expansion is equal to

$$l_1 = p_2(v_3 - v_2) + \frac{1}{k-1}(p_3 v_3 - p_4 v_4) = 66.2 \times 10^5 (0.1 - 0.05) +$$

$$+ \frac{10^5}{0.4}(66.2 \times 0.1 - 2.64 \times 1) = 1\,326\,000 \text{ J/kg} = 1326 \text{ kJ/kg}.$$

The work of compression amounts to

$$l_1=\frac{1}{k-1}(p_1v_1-p_2v_2)=\frac{10^5}{0.4}(1-66.2\times0.05)=$$

$$=-578\ 000\ \text{J/kg}=-578\ \text{kJ/kg}.$$

The useful work is determined to be

$$l=l_1+l_2=1326-578=748\ \text{kJ/kg}.$$

The quantity of heat added to the working medium is

$$q_1=c_p(T_3-T_2)=\frac{29.09}{28.85}(2310-1155)=1162\ \text{kJ/kg}.$$

The quantity of rejected heat is equal to

$$q_2=c_v(T_4-T_1)=\frac{20.78}{28.85}(920-350)=410\ \text{kJ/kg}.$$

The usefully employed heat is equal to

$$q=q_1-q_2=1162-410=752\ \text{kJ/kg}.$$

The thermal efficiency of the cycle is

$$\eta_t=\frac{q}{q_1}=\frac{752}{1162}=0.648.$$

Checking the thermal efficiency of the cycle

$$\eta_t=1-\frac{\varrho^k-1}{k\varepsilon^{k-1}}(\varrho-1)=1-\frac{2^{1.4}-1}{1.4\times20^{0.4}}=0.65.$$

In accordance with the assumed conditions, the thermal efficiency of the Carnot cycle is equal to

$$\eta_t=1-\frac{T_1}{T_3}=1-\frac{350}{2310}=0.85$$

The mean indicator pressure is equal to

$$p_i=\frac{l}{v_1-v_2}=\frac{748\ 000}{(1-0.05)\times10^5}=7.88\ \text{bar}.$$

Example 17-3. A reciprocating internal dual combustion engine (Fig. 17-6) is operated at an initial pressure $p_1=1$ bar, initial temperature $t_1=27$ °C, a compression ratio $\varepsilon=12.7$, pressure ratio $\lambda=1.4$ and a degree of preliminary expansion $\varrho=1.6$. The working medium is air with a gas constant $R=287$ J/kg·deg; heat capacities are assumed to be constant: $c_v=0.72$ kJ/kg·deg, $c_p=1.01$ kJ/kg·deg; the adiabatic exponent $k=1.4$.

Determine the parameters of state at the characteristic points, the work of compression, the work of expansion and the useful work, the thermal efficiency of the cycle, the amount of delivered and rejected heat the thermal efficiency of the Carnot cycle based on problem conditions, the mean indicator pressure. Calculations should be made per 1 kg of air.

Parameters at point *1:*

the initial volume, v_1, is determined from the equation of state:

$$v_1=\frac{RT_1}{p_1}=\frac{287\times300}{1\times10^5}=0.86 \text{ m}^3/\text{kg};$$

$p_1=1$ bar; $t_1=27$ °C.

Parameters at point *2:*

since the compression ratio $\varepsilon=\frac{v_1}{v_2}=12.7$, then

$$v_2=\frac{v_1}{\varepsilon}=\frac{0.86}{12.7}=0.0678 \text{ m}^3/\text{kg};$$

the temperature at the end of adiabatic compression

$$T_2=T_1\left(\frac{v_1}{v_2}\right)^{k-1}=300\times12.7^{0.4}=300\times2.76=828 \text{ K};$$

the pressure at the end of adiabatic compression

$$p_2=\frac{RT_2}{v_2}=\frac{287\times828}{0.0678\times10^5}=35.0 \text{ bar}.$$

Parameters at point *3:*

from the ratio of parameters in an isochoric process we obtain

$v_3=0.0678$ m³/kg; $p_3=p_2\lambda=35\times1.4=49.0$ bar;

$T_3=T_2\lambda=828\times1.4=1160$ K.

Parameters at point *4:*

from the ratio of parameters in an isobaric process we obtain

$p_4=49.0$ bar; $v_4=v_3\varrho=0.0678\times1.6=0.1085$ m³/kg;

$T_4=T_3\varrho=1160\times1.6=1858$ K.

Parameters at point *5:*

$v_5=v_1=0.86$ m³/kg;

the pressure at the end of adiabatic expansion

$$\frac{p_4}{p_5}=\left(\frac{v_5}{v_4}\right)^k=\left(\frac{v_1}{v_4}\right)^k=\left(\frac{0.86}{0.1085}\right)^{1.4}=18.2;$$

$$p_5=\frac{49.0}{18.2}=2.7 \text{ bar};$$

the temperature at the end of adiabatic expansion

$$T_5=T_1\left(\frac{p_5}{p_1}\right)=300\left(\frac{2.7}{1}\right)=808 \text{ K}.$$

The work input of the cycle can be determined as the difference between the work of expansion and work of compression.

The work of compression is equal to

$$l_1=\frac{1}{k-1}(p_1v_1-p_2v_2)=\left(\frac{10^5}{0.4}\right)(1\times0.86-35\times0.0678)=$$

$$=-380\,000\ \text{J/kg}=-380\ \text{kJ/kg}.$$

The work of expansion amounts to

$$l_2=\frac{1}{k-1}(p_4v_4-p_5v_5)+p_3(v_4-v_3)=\left(\frac{10^5}{0.4}\right)\times(49.0\times0.1085-2.7\times0.86)+$$

$$+49.0\times10^5(0.1085-0.0678)=948\,000\ \text{J/kg}=948\ \text{kJ/kg}.$$

The work input of the cycle is equal to the algebraic sum of l_1 and l_2,

$$l=l_2-l_1=955-380=575\ \text{kJ/kg}.$$

The quantity of added heat

$$q_1'=c_v(T_3-T_2)=0.72(1160-828)=238\ \text{kJ/kg};$$

$$q_1''=c_p(T_4-T_3)=1.01(1858-1160)=705\ \text{kJ/kg}.$$

The quantity of rejected heat

$$q_2=c_v(T_5-T_1)=0.72(808-300)=366\ \text{kJ/kg}.$$

The usefully employed heat in the cycle

$$q=q_1'+q_2''-q_2=238+705-366=577\ \text{kJ/kg}.$$

The thermal efficiency of the cycle is equal to

$$\eta_t=\frac{577}{948}=0.61;$$

$$\eta_t=1-\frac{\lambda\varrho^k-1}{\varepsilon^{k-1}(\lambda-1)+k\lambda(\varrho-1)}=1-\frac{1.4\times1.6^{1.4}-1}{12.7^{0.4}[(1.4-1)+1.4\times1.4(1.6-1)]}=0.61.$$

By the conditions of the problem the thermal efficiency of the Carnot cycle

$$\eta_t=1-\frac{300}{1858}=0.838.$$

The mean indicator pressure is equal to

$$p_i=\frac{l}{v_1-v_2}=\frac{575\,000}{10^5(0.86-0.0678)}=7.25\ \text{bar}.$$

CHAPTER EIGHTEEN

CYCLES OF GAS-TURBINE PLANTS AND REACTION ENGINES

18-1. Gas-Turbine Plants

The main shortcomings of reciprocating internal combustion engines are the limitation in developed power and the fact that it is impossible to realize adiabatic expansion of the working medium to atmospheric pressure. These drawbacks are foreign to gas-turbine plants, using as a working medium the products of combustion of liquid or gaseous fuel. The working medium, at a high temperature and pressure, flows from the combustion chamber to a nozzle where it expands and passes from there at a still higher velocity to the blades of the gas turbine, where the kinetic energy of the working medium is used to obtain mechanical work.

Gas-turbine plants possess many important advantages over reciprocating engines. Gas turbines are of a comparatively small weight and size, they incorporate no reciprocating parts, and they can be constructed to be operated at high speeds (rpm) with high power ratings per single unit.

However in the creation of high-power stationary gas-turbine plants a number of essential and important problems have to be solved. For one thing it is necessary to raise substantially the initial gas temperature at the turbine inlet, so as to raise the thermal efficiency of the gas turbine. This problem calls for the creation of new grades of high-temperatures steel, capable of stable and continuous performance under maximum temperatures. The presently practised water- or gas-cooling of elements of gas turbines subjected in operation to high temperatures, is insufficiently reliable and the cooling appliances are of intricate construction.

Another problem to be solved is the creation of a small-size, compact, regenerative gas-air heat exchanger which, as it will be made clear below, must be an integral component part of a modern efficient gas-turbine plant.

Of essential importance for the efficiency of a gas-turbine plant is an increase of the effective efficiency of the compressor which is a component part of any gas-turbine plant. About 75 per cent of the capacity of a gas turbine is expended to drive the compressor and that is why the overall effective, or thermal, efficiency of a gas-turbine plant is mainly determined by the degree of perfection of compressor performance. But, in general, the gas turbine is a very promising engine and its wide introduction to industrial applications is of very great importance.

Gas turbines can be operated with fuel combustion at constant pressure or at constant volume. The respective ideal cycles of these gas turbines are classified as cycles with heat addition at a constant pressure or at a constant volume.

18-2. Cycles of Constant-Pressure Combustion Gas Turbines

Shown in Fig. 18-1 is the schematic diagram of the simplest constant-pressure combustion-gas turbine. Air from the turbocompressor *4* and fuel from the fuel pump *5* are delivered continuously into the combustion chamber *1* through injectors *6* and *7*. From the combustion chamber the products of combustion are directed to the combined nozzles *2* in which

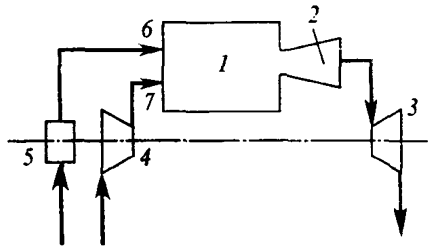


FIG. 18-1

the working medium expands to a pressure close to atmospheric pressure. From the nozzles the products of combustion reach the blades of the gas turbine *3* and are then discharged into the atmosphere through an exhaust duct.

The ideal cycle of the gas-turbine plant is represented on the *p-v* and *T-s* diagrams shown in Figs. 18-2 and 18-3. In this cycle heat is rejected from the working medium not along an isochor, as is the case with reciprocating internal combustion engines, but along an isobar. In reciprocating internal

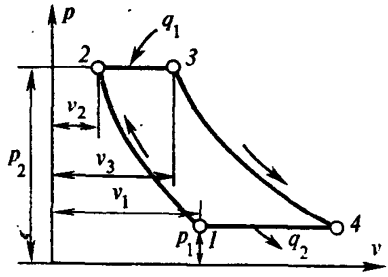


FIG. 18-2

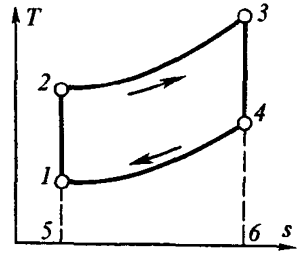


FIG. 18-3

combustion engines the volume of the expanding gases is restricted by the swept volume or piston displacement. No such restriction exists in gas turbines and the gases are free to expand to atmospheric pressure.

The working medium with initial parameters p_1, v_1, T_1 is compressed along adiabat *1-2* to point *2*. From here a certain quantity of heat q_1 is added to the working medium along isobar *2-3*. Then the working medium expands adiabatically along line *3-4* to its initial pressure and returns along isobar *4-1* into its initial state in which heat q_2 is rejected from it.

The characteristics of the cycle are: the pressure ratio of the compressor, $\beta=\frac{p_2}{p_1}$, and the degree of preliminary (isobaric) expansion $\varrho=\frac{v_3}{v_2}$.

The quantity of added heat is determined by formula

$$q_1=c_p(T_3-T_2),$$

and the quantity of rejected heat—by the following formula:

$$q_2=c_p(T_4-T_1).$$

The thermal efficiency of the cycle is equal to

$$\eta_t=1-\frac{q_2}{q_1}=1-\frac{c_p(T_4-T_1)}{c_p(T_3-T_2)}=1-\frac{T_4-T_1}{T_3-T_2}.$$

Let us express the temperatures T_2, T_3 and T_4 in terms of the initial temperature of the working medium, T_1

for the adiabat *1-2*

$$\frac{T_2}{T_1}=\left(\frac{p_2}{p_1}\right)^{(k-1)/k}=\beta^{(k-1)/k};\quad T_2=T_1\beta^{(k-1)/k};$$

for the isobar *2-3*

$$\frac{T_3}{T_2}=\frac{v_3}{v_2}=\varrho;\quad T_3=T_2\varrho;\quad T_3=T_1\beta^{(k-1)/k}\varrho;$$

for the adiabat *3-4*

$$\frac{T_4}{T_3}=\left(\frac{p_4}{p_3}\right)^{(k-1)/k}=\left(\frac{p_1}{p_2}\right)^{(k-1)/k}=\left(\frac{p_1}{p_1\beta}\right)^{(k-1)/k}=\frac{1}{\beta^{(k-1)/k}};$$

$$T_4=T_1\beta^{(k-1)/k}\varrho\frac{1}{\beta^{(k-1)/k}}=T_1\varrho.$$

Substituting the values of the temperatures obtained into the equation for the thermal efficiency, we obtain

$$\eta_t=1-\frac{T_1\varrho-T_1}{T_1\beta^{(k-1)/k}\varrho-T_1\beta^{(k-1)/k}}=1-\frac{\varrho-1}{\beta^{(k-1)/k}(\varrho-1)} \qquad (18\text{-}1)$$

or

$$\eta_t=1-\frac{1}{\beta^{(k-1)/k}}.$$

The thermal efficiency of a gas-turbine plant in which heat is added at a constant pressure depends on the compressor pressure ratio β and on the adiabatic exponent k, the efficiency rising with these quantities.

After the gas turbine it is expendient to direct the exhaust gas into a heat exchanger to heat the air delivered into the combustion chamber or use the exhaust gas to produce hot water, steam, etc. for communal heating.

With the aid of the *T-s* diagram the thermal efficiency of a constant-

pressure combustion gas-turbine is determined from the ratio of areas (Fig. 18-3)

$$\eta_t = \frac{\text{area } 5236 - \text{area } 5146}{\text{area } 5236} = \frac{\text{area } 1234}{\text{area } 5236}.$$

When considering the performance of real gas-turbine plants it is also necessary to take account of the losses due to the irreversible nature of the processes proceeding in the turbo-compressor and in the gas turbine proper.

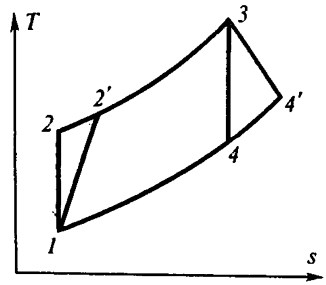


FIG. 18-4

The energy expended in the compressor to overcome friction involves an increase in the temperature of the working medium, since the work of friction turns into heat, which is transferred to the working medium, and this in turn leads to an increase of the quantity of work expended to compress the air (the loss of heat to the surroundings by radiation is ignored here). It is clear from Fig. 18-4 that the theoretical cycle of a constant-pressure combustion gas-turbine plant to which heat is added at $p = \text{const}$ is represented on the *T-s* diagram by area *12341*, and the real cycle—by area *12'34'1*, where line *1-2'* represents the conventional process of irreversible adiabatic compression in the compressor, and line *3-4'* represents conventionally the process of irreversible adiabatic expansion in the turbine.

The theoretical amount of work spent to compress air in the compressor is $l_{ad}^c = i_2 - i_1$, and the real work of compression is equal to $l_i^c = i_{2'} - i_1$, or

$$l_i^c = \frac{l_{ad}^c}{\eta_{ad}^c} = \frac{i_2 - i_1}{\eta_{ad}^c} \qquad (18\text{-}2)$$

where η_{ad}^c is the adiabatic efficiency of the compressor, equal to the ratio

$$\eta_{ad}^c = \frac{i_2 - i_1}{i_{2'} - i_1}.$$

At the present time the efficiency η_{ad}^c approaches 0.8 to 0.85.

The expansion of the gas as it flows through the turbine blading and nozzles is accompanied by losses due to friction against the walls of the nozzles and the blades, and due to swirling of the flow, resulting in a fraction of the kinetic energy of the working medium turning into heat so that the enthalpy of the gas at the turbine outlet, $i_{4'}$, is greater than the enthalpy involved in a reversible process of expansion, i_4. The theoretical work of expansion in the gas turbine is equal to $l_t = i_3 - i_4$, and the real work of expansion $l_i^t = i_3 - i_{4'}$.

The ratio of the internal real work of expansion realized in a real gas turbine to the theoretical work output of an ideal turbine is referred to as the *internal relative efficiency of a gas turbine*

$$\eta_{turb} = \frac{l_i^t}{l_t} = \frac{i_3 - i_{4'}}{i_3 - i_4} \qquad (18\text{-}3)$$

The better and more perfect the design of the turbine blading, the lesser the losses suffered in the turbine due to gas friction and eddies and the higher the turbine efficiency η_{turb}. The efficiency of modern gas turbines is within 0.8-0.9.

The real useful work output that can be realized in a gas-turbine plant, l_{real}, is equal to the difference between the real work of expansion and the real work of compression

$$l_{real}=(i_3-i_4)\eta_{turb}\eta_{mech}-\frac{i_2-i_1}{\eta_{ad}^c}$$

where η_{mech} is the mechanical efficiency.

The ratio of the useful work output of a gas-turbine plant, l_{real}, to the quantity of heat spent, $q_{1\,real}$, is called the *actual efficiency of the gas-turbine plant*

$$\eta=\frac{l_{real}}{q_{1\,real}}=\frac{(i_3-i_4)\eta_{turb}\eta_{mech}-(i_2-i_1)\eta_{ad}^c}{i_3-i_{2'}}. \qquad (18\text{-}4)$$

A detailed analysis of the equation derived can be found in special literature devoted to gas-turbine plants.

18-3. Cycles of Constant-Volume Combustion Gas Turbines

Shown in Fig. 18-5 is the schematic diagram of a constant-volume combustion gas-turbine plant. In a plant of this kind the air compressed in turbocompressor *6* flows from receiver *7* (a vessel of large capacity used

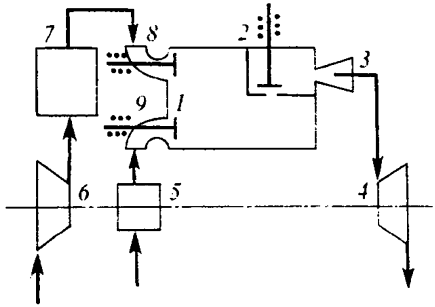


FIG. 18-5

to equalize pressure) through air valve *8* into combustion chamber *1*, into which fuel pump *5* delivers liquid fluid via the fuel valve *9*. The products of combustion, flowing through nozzle valve *2*, expand in nozzle *3* and impart rotational motion to the rotor *4* of the gas turbine.

To realize periodic fuel combustion air and fuel must be delivered into the combustion chamber through controlled valves *8* and *9* in definite time intervals. Combustion takes place when valves *2* and *8* are closed. The fuel

is ignited from an electric spark. Upon completion of fuel combustion, pressure in combustion chamber *1* rises, the nozzle valve *2* opens and the products of combustion pass to the nozzle *3* where they expand to the final pressure.

The *p-v* and *T-s* diagrams shown in Figs. 18-6 and 18-7 present an ideal cycle of a gas-turbine plant in which heat is added to the working medium at $v=\text{const}$. The working medium, whose initial parameters are p_1, v_1, T_1, is compressed adiabatically along line *1-2* to point *2*, the pressure at which is determined by the pressure ratio. Then a certain amount of heat q_1 is added to the working medium isochorically along line *2-3* and after that

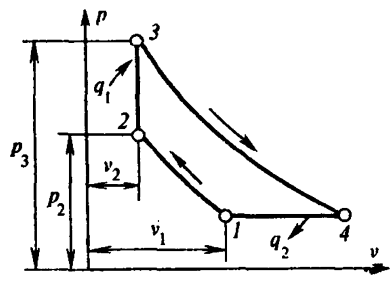


FIG. 18-6

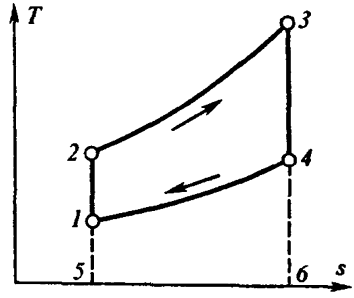


FIG. 18-7

the working medium expands along adiabat *3-4* to the initial pressure (point *4*) and returns to its initial state along isobar *4-1* with the quantity of heat, q_2, being rejected from the working medium.

The characteristics of the cycle are the compressor pressure ratio $\beta=p_2/p_1$ and the additional pressure ratio $\lambda=p_3/p_2$.

The quantity of added heat is determined by formula

$$q_1=c_v(T_3-T_2),$$

and the amount of rejected heat—by formula

$$q_2=c_p(T_4-T_1).$$

Substituting the values of q_1 and q_2 into the expression for the thermal efficiency of the cycle, we obtain

$$\eta_t=1-\frac{q_2}{q_1}=1-\frac{c_p(T_4-T_1)}{c_v(T_3-T_2)}=1-\frac{k(T_4-T_1)}{T_3-T_2}.$$

Let us express the temperatures T_2, T_3 and T_4 in terms of the initial temperature of the working medium, T_1

for the adiabat *1-2*

$$\frac{T_2}{T_1}=\left(\frac{p_2}{p_1}\right)^{(k-1)/k}=\beta^{(k-1)/k};$$

$$T_2=T_1\beta^{(k-1)/k};$$

for the isochor *2-3*

$$\frac{T_3}{T_2}=\frac{p_3}{p_2}=\lambda; \quad T_3=T_2\lambda \quad \text{and} \quad T_3=T_1\beta^{(k-1)/k}\lambda;$$

for the adiabat *3-4*

$$\frac{T_4}{T_3}=\left(\frac{p_4}{p_3}\right)^{(k-1)/k}=\left(\frac{p_1}{p_1\beta\lambda}\right)^{(k-1)/k}=\frac{1}{(\beta\lambda)^{(k-1)/k}},$$

$$T_4=T_3\left(\frac{1}{\beta\lambda}\right)^{(k-1)/k}=T_1\beta^{(k-1)/k}\lambda\left(\frac{1}{\beta\lambda}\right)^{(k-1)/k} \quad \text{and} \quad T_4=T_1\lambda^{1/k}$$

Let us substitute the obtained temperatures into the expression for the thermal efficiency of the cycle. Then

$$\eta_t=1-\frac{k(T_4-T_1)}{(T_3-T_2)}=1-\frac{k(T_1\lambda^{1/k}-T_1)}{T_1\beta^{(k-1)/k}\lambda-T_1\beta^{(k-1)/k}},$$

or

$$\eta_t=1-\frac{k(\lambda^{1/k}-1)}{\beta^{(k-1)/k}(\lambda-1)}. \tag{18-5}$$

The thermal efficiency of a constant-volume combustion gas turbine with heat addition at $v=\text{const}$ depends on the quantities k, β and λ and it increases with them.

On the *T-s* diagram the thermal efficiency of the constant-volume gas turbine at $v=\text{const}$ is determined from the ratio of the areas representing the added and rejected amounts of heat (Fig. 18-7)

$$\eta_t=\frac{\text{area } 5236-\text{area } 5146}{\text{area } 5236}=\frac{\text{area } 1234}{\text{area } 5236}.$$

18-4. Comparison of Cycles of Gas-Turbine Plants

Shown in Fig. 18-8 are the cycles of gas-turbine plants realized at the same compressor pressure ratios and the same maximum temperatures. It is clear from the illustration that the cycle of a constant-volume combustion gas turbine in which heat is added at $v=\text{const}$ has the highest efficiency.

In fact, it is clear from Fig. 18-8 that in the cycle at $v=\text{const}$ the integral mean temperature T'_v, at which heat is added, will be higher and the integral mean temperature T''_v, at which heat is rejected, will be lower than in the cycle of a constant-pressure combustion engine with heat addition at $p=\text{const}$

$$\eta_{tp\text{-}const}>\eta_{tv\text{-}const}.$$

A comparison of gas-turbine cycles realized at different compressor pressure ratios and the same maximum temperatures corroborates the conclusion arrived at in investigating the performance of reciprocating internal combustion engines that the cycle involving heat addition at $p=\text{const}$ shall have a higher efficiency than the cycle realized with heat addition at $v=\text{const}$,

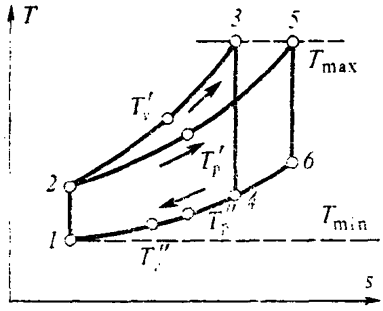


FIG. 18-8

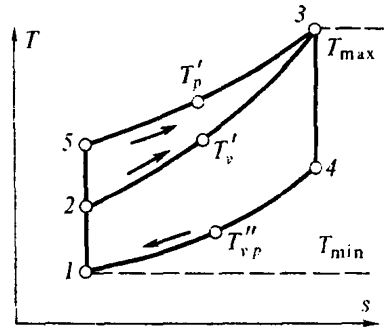


FIG. 18-9

i.e. the cycle efficiency determined by the method of integral mean temperatures is higher for constant-pressure combustion gas-turbine plants (Fig. 18-9)

$$\eta_{tp\text{-}const} > \eta_{tv\text{-}const}.$$

18-5. Methods of Increasing the Efficiency of Gas-Turbine Plants

The thermal efficiency of a constant-pressure combustion gas turbine increases with an increase of the compressor pressure ratio β. However, an increase in β causes an increase of the temperature of combustion products at the end of fuel combustion, T_3, resulting in a more rapid deterioration of turbine blades and nozzles, the cooling of which is hampered.

To raise the efficiency of gas-turbine plants their operating conditions have been partly changed. For this purpose gas-turbine plants have been introduced with heat regeneration, multistage air compression in the compressor, and multistage combustion, etc. All these measures have yielded a considerable effect and raised the degree of perfection with which heat was converted into work in gas-turbine plants.

Let us investigate in some greater detail the application of heat regeneration in constant-pressure combustion gas turbines (Fig. 18-10). From the turbocompressor *4* compressed air is directed to flow into the regenerator (heat exchanger) *8* where the air is heated at a constant pressure by the

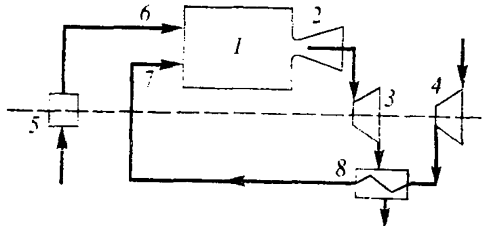


FIG. 18-10

gases flowing from the combustion chamber *1* through nozzle *2* into the gas turbine *3*. From the regenerator *8* heated air flows through injector *7*, and fuel from the fuel pump *5* via injector *6* flows into the combustion chamber *1*.

The ideal cycle of such a gas-turbine plant with regeneration of heat is shown in Figs. 18-11 and 18-12.

In these illustrations: line *1-2* represents adiabatic air compression in the compressor; line *2-5*—isobaric heat addition in the regenerator; *5-3*—heat addition at a constant pressure in the combustion chamber; line *3-4*—adiabatic expansion of the combustion products in turbine nozzles; line *4-6*—isobaric rejection of heat from the gases in the regenerator;

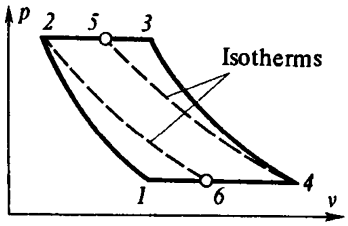


FIG. 18-11

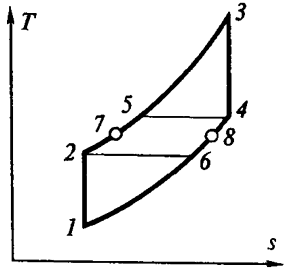


FIG. 18-12

6-1—isobaric rejection of heat from the gases to the low-temperature source after the regenerator.

Should we assume that the gases are cooled in the regenerator to the temperature of the air flowing into it, i.e. from T_4 to $T_6=T_2$, complete regeneration shall take place.

With complete regeneration, when $T_4-T_6=T_5-T_2$, the thermal efficiency of the cycle is determined by equation

$$\eta_t=1-\frac{q_2}{q_1},$$

where

$$q_1=c_p(T_3-T_5)=c_p(T_3-T_4),$$

and

$$q_2=c_p(T_6-T_1)=c_p(T_2-T_1),$$

then

$$\eta_t=1-\frac{T_2-T_1}{T_3-T_4}.$$

The temperature at the main points of the cycle are determined as follows:

$$T_2=T_1\left(\frac{p_2}{p_1}\right)^{(k-1)/k}=T_1\beta^{(k-1)/k};$$

$$T_3=T_1\beta^{(k-1)/k}\varrho; \quad T_4=T_1\varrho.$$

The thermal efficiency of the cycle

$$\eta_{t\,reg}=1-\frac{1}{\varrho}=1-\frac{T_1}{T_4}. \tag{18-6}$$

The thermal efficiency of a constant-pressure combustion cycle realized with complete heat regeneration depends on the initial gas temperature T_1 and on the temperature T_4 of the gas at the end of adiabatic expansion.

It is practically impossible to realize complete regeneration due to the restricted size of the regenerators, or heat exchangers, and the presence of a finite difference between the temperatures of the heated and cooled gas flows. In this case the temperature of the air heated in the regenerator shall be T_7, somewhat lower than T_5, and the temperature of the cooled gases—T_8, higher than T_6. That is why the thermal efficiency of the cycle must depend on the degree of regeneration which is determined as the ratio of temperatures

$$\sigma=\frac{T_7-T_2}{T_5-T_2}=\frac{T_4-T_8}{T_4-T_6}=\frac{T_4-T_8}{T_5-T_2}. \tag{18-7}$$

The thermal efficiency of a gas-turbine operated with incomplete regeneration, i.e. with $\sigma<1$, is determined as follows:

$$\eta_{t\,reg}=1-\frac{T_4-T_1-\sigma(T_5-T_2)}{T_3-T_2-\sigma(T_5-T_2)}. \tag{18-8}$$

The degree of regeneration depends on the design of the heat exchanger (regenerator) or size of the heat-transfer surfaces.

Regeneration of heat can also be accomplished in a constant-volume combustion gas-turbine plant. Inasmuch as regeneration proceeds in the heat exchanger at a constant pressure, heat is then added both isobarically and isochorically (Fig. 18-13). This cycle consists of the following processes: line *1-2*—adiabatic air compression in the compressor; line *2-3*—heating of the compressed air in the regenerator at $p=\text{const}$; line *3-4*—heat addition at $v=\text{const}$ in the combustion chamber; line *4-5*—adiabatic expansion of the products of combustion in the nozzles of the gas turbine; line *5-6*—rejection (removal) of heat from the gases in the regenerator at $p=\text{const}$; and line *6-1* represents the process of heat rejection from the gases to a low-temperature source at $p=\text{const}$.

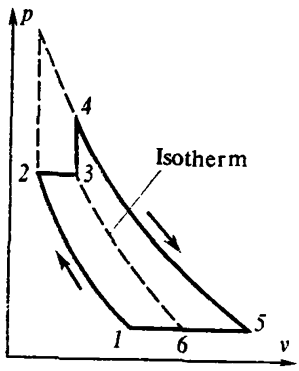


FIG. 18-13

The quantities of the added and rejected heat shall be

$$q_1=c_v(T_4-T_3); \quad q_2=c_p(T_5-T_1)=c_p(T_3-T_2).$$

The thermal efficiency of the cycle considered is equal to

$$\eta_t=1-\frac{q_2}{q_1}=1-\frac{k[(T_5-T_1)-(T_3-T_2)]}{T_4-T_3}. \tag{18-9}$$

As a result of heat regeneration cycle the thermal efficiency of a constant-volume combustion gas-turbine also increases. Regeneration of heat in a gas turbine permits a reduction of the maximum cycle pressure without a drop of efficiency.

In addition, the efficiency of a gas-turbine plant can be raised by using isothermal addition and rejection of heat. In practice, however, isothermal compression and isothermal addition of heat cannot be fully realized due to the design difficulties involved. The actual process of compression is made close to isothermal in compressors by practising multistage compression with intercooling. Just as in compressors, in gas turbines the actual process of heat addition is made close to isothermal by introducing stepped, or multistage combustion with the products of combustion expanding in individual turbine stages. The more stages there are of expansion and compression, the higher is the thermal efficiency of a gas turbine. But it is inexpedient to use a great number of combustion chambers and intercoolers, since this greatly complicates the design of the gas-turbine plant and increases the losses due to the irreversibility of the processes.

On the basis of economic production indices, it is common practice to construct gas-turbine plants using two-stage expansion and three-stage compression. In a plant of this kind atmospheric air is compressed successively in individual stages of the compressor and cooled in the intercoolers provided between stages. The air, compressed to a high pressure, passes into the first combustion chamber where it is heated to maximum temperature. Upon expansion in the gas turbine the working medium, gas, flows into the second combustion chamber where it is again heated to the maximum temperature as a result of constant-pressure fuel combustion. Then, the products of combustion expand in a second turbine (or in the second stage of the first turbine) and are discharged into the atmosphere. If the gas-turbine plant is operated on the heat regeneration cycle, the compressed air can be heated at the expense of the heat contained in the exhaust gases.

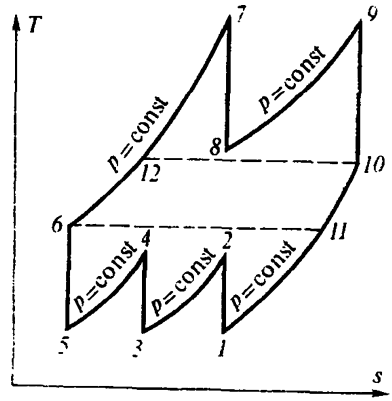


FIG. 18-14

The ideal cycle of such a gas-turbine plant is represented on the *T-s* diagram shown in Fig. 18-14.

The use of regeneration of heat, stepped compression, stepped heat addition, raises considerably the efficiency of gas-turbine plants, at that the ideal cycle approaches the generalized (regenerative) Carnot cycle.

All real gas-turbine plants are operated on an open cycle. In such open-cycle machines, upon performing work on the turbine blades, the products

of combustion are discharged to the atmosphere. Liquid or gaseous fuel is employed, containing a minimal number of solid particles, so as to prevent untimely wear of turbine blades.

Solid fuel-fired gas-turbine plants are operated on the closed cycle. In such machines the working medium is clean air or another gas heated in surface-type heat exchangers. A given quantity of air or gas passes through the gas turbine and the heat exchangers, so that the working medium undergoes a closed process.

The closed process possesses a number of advantages. It can be realized with cheap solid fuels and air can be used at higher pressures, resulting in a decrease of the volume of the working medium and, consequently, of the size of the plant. In gas-turbine plants of this kind atmospheric air is replaced by heavier gases and low-boiling substances, carbon dioxide, for instance. The use of carbon dioxide, instead of air, permits the compressor to be replaced by a pump which raises the efficiency and reliability of the plant. The main disadvantage of closed-cycle gas-turbine plants is the large size of the heat exchangers.

18-6. Reaction-Engine Cycles

At the end of the Second World War reaction engines appeared in aviation. Aeroplanes powered with reciprocating engines are capable of flying at a maximum speed of up to 800 km/h, while the speed of aircraft with reaction engines may be 3000 km/h and even this speed is not the limit for such aircraft.

Such a difference in speed is traced to the fact that, compared with piston, or reciprocating, engines, reaction engines are capable of developing enormous power with a comparatively small weight and simple construction.

Machines of this kind are referred to as reaction engines because the energy of fuel is converted into the kinetic energy of a jet of gas and the resulting reaction force is made use of as thrust that is equal to

$$p = m(w_g - w_a),$$

where m = mass of combustion products forming per 1 s, kg/s;
w_g = velocity of gas at the nozzle exit;
w_a = aircraft flight speed.

These days turboprop engines with a combined thrust, from the propeller and from the reaction of the gas jet leaving the nozzle, are widely used.

Air-breathing reaction engines, depending on the process of heat addition, can be divided into constant-pressure combustion *ramjet* engines and constant-volume combustion *pulse-jet* engines. They may also be of either *compressorless* or *turbocompressor design.*

The ideal cycles of air-breathing reaction engines are similar to those of constant-volume combustion and constant-pressure combustion gas-turbine plants.

Shown in Fig. 18-15 is the schematic diagram of a constant-pressure combustion ramjet-type air-breathing engine. The engine consists of a diffuser *1*, where air is compressed, and a combustion chamber *2* into which fuel is introduced through a number of injectors. The combustible mixture is ignited by an electric spark. The gases leave the engine through the reaction, or propelling, nozzle *3* in which gas pressure drops to atmospheric. The compression ratio ensured by the diffuser is not very great and that is why the efficiency of the engine is sufficiently high only at high flight speeds.

In turbocompressor engines or turbojet engines, as they are called, air, after compression in the diffuser, is additionally compressed in the turbocompressor that is rotated by the gas turbine located downstream of the combustion chamber. Due to the greater compression ratio the efficiency of turbojet engines is considerably higher than that of compressorless engines even at comparatively low aircraft flight speeds. This explains why turbojet engines find wide application in modern aviation. From the thermodynamic viewpoint these two engines do not differ essentially from each other.

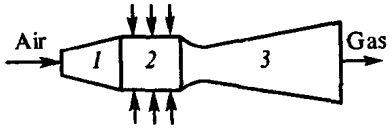


FIG. 18-15

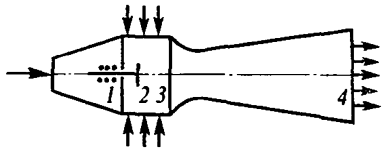


FIG. 18-16

The ideal cycles realized in air-breathing ramjet and turbojet engines are the same as in constant-pressure combustion gas-turbine plants (see Sec. 18-2). Consequently, the thermal efficiency of an air-breathing reaction engine is equal to

$$\eta_t = 1 - \frac{1}{\beta^{(k-1)/k}}$$

Shown in Fig. 18-16 is the schematic diagram of a constant-pressure combustion air-breathing pulse-jet engine. The air compressed in diffuser *1* is directed to combustion chamber *3* into which simultaneously fuel is injected. Upon filling of the combustion chamber, valves *2*, separating the diffuser from the combustion chamber, close and the combustible mixture is ignited by an electric spark. Combustion proceeds at a high rate and is represented by an isochor in the cycle. Upon completion of mixture combustion the nozzle valve (not shown in the illustration) opens, the products of combustion expand in nozzle *4* from which the gases are discharged to the atmosphere. Then, the working process repeats.

Characteristic of the performance of this type of reaction engine is the fact that the combustion chamber is periodically separated from the nozzle, pulsing is observed and that is why the machine is referred to as a pulse-jet engine.

The ideal cycle of an air-breathing pulse-jet engine realizing constant-volume fuel combustion does not differ from that of a constant-volume

combustion gas-turbine plant and that is why the thermal efficiency of this engine is determined by Eq. (18-5)

$$\eta_t = 1 - \frac{k(\lambda^{1/k} - 1)}{\beta^{(k-1)/k}(\lambda - 1)}$$

In air-breathing pulse-jet engines the pressure at the end of fuel combustion is considerably higher than that in ramjet engines, therefore their efficiency is higher. However, because of their intricate construction and periodic nature performance pulse-jet engines have not found wide application.

Typical Questions and Examples to Chapter Eighteen

1. What necessitated the creation of gas turbines and reaction engines?
2. What are the shortcomings of piston (reciprocating) internal combustion engines?
3. What are the merits of gas turbines and reaction engines?
4. Give a description of the principle of operation of a constant-pressure combustion gas-turbine plant.
5. Give a description of the ideal cycle of a constant-pressure combustion gas-turbine plant.
6. Derive the expression (formula) for the thermal efficiency of a cycle with constant-pressure heat addition.
7. How is the cycle of a constant-pressure combustion gas-turbine plant represented on p-v and T-s diagrams?
8. Describe the design and performance cycle of a constant-volume combustion gas-turbine plant.
9. Describe the ideal cycle of a constant-volume combustion gas-turbine plant.
10. Derive the expression (formula) for the thermal efficiency of a cycle with constant-volume heat addition.
11. How is the cycle of a constant-volume combustion gas-turbine plant represented on p-v and T-s diagrams?
12. Compare cycles of gas-turbine plants.
13. What are the methods of raising the thermal efficiency of gas-turbine plants?
14. What is meant by a reaction engine?
15. Describe the ideal cycles of reaction engines.
16. Into what groups are reaction engines divided and in what way do the groups of engines differ from each other?

Example 18-1. For an ideal cycle of a gas-turbine plant with heat addition at $p = \text{const}$ determine the following parameters at the characteristic points: the work of expansion, the work of compression and the useful work; the quantities of added and rejected heat; the thermal efficiency of the cycle. The initial properties of the working medium are: $p_1 = 1$ bar; $T_1 = 300$ K; pressure ratio of the process of compression in the compressor

realizing adiabatic compression, $\beta=p_2/p_1=10$; adiabatic exponent $k=1.4$. The temperature at point *3* should not exceed 1000 K; the working medium is air of a constant heat capacity; calculation should be carried out per 1 kg of the working medium.

Specific volume of the working medium at point *1*

$$v_1=\frac{RT_1}{p_1}=\frac{287\times300}{10^5}=0.86 \text{ m}^3/\text{kg}.$$

Parameters at point 2:

$$p_2=p_1\times10=10 \text{ bar};$$

$$\frac{T_2}{T_1}=\left(\frac{p_2}{p_1}\right)^{(k-1)/k}; \quad T_2=300\times10^{0.286}=580 \text{ K};$$

$$v_2=\frac{RT_2}{p_2}=\frac{287\times580}{10\times10^5}=0.1665 \text{ m}^3/\text{kg}.$$

Parameters at point *3*:

$$p_3=10 \text{ bar}; \quad T_3=1000 \text{ K};$$

$$v_3=\frac{RT_3}{p_3}=\frac{287\times1000}{10\times10^5}=0.287 \text{ m}^3/\text{kg}.$$

Parameters at point *4*:

$$p_4=1 \text{ bar};$$

$$\frac{v_4}{v_3}=\left(\frac{p_3}{p_4}\right)^{1/k}; \quad v_4=0.287\times10^{0.714}=1.488 \text{ m}^3/\text{kg};$$

$$T_4=\frac{p_4v_4}{R}=\frac{10^5\times1.488}{287}=518 \text{ K}.$$

The work of compression

$$l_1=p_1(v_4-v_1)+\frac{1}{k-1}(p_2v_2-p_1v_1)=10^5(1.488-0.86)+$$

$$+\frac{10^5}{0.4}(10\times0.1665-0.86)=263\,500 \text{ J/kg}=263.5 \text{ kJ/kg}.$$

The work of expansion

$$l_2=p_2(v_3-v_2)+\frac{1}{k-1}(p_3v_3-p_4v_4)=10\times10^5(0.287-0.1665)+$$

$$+\frac{10^5}{0.4}(10\times0.287-1.488)=466\,500 \text{ J/kg}=466.5 \text{ kJ/kg}.$$

The useful work

$$l=l_2-l_1=466.5-263.5=203 \text{ kJ/kg}.$$

The amount of added heat

$$q_1=c_p(T_3-T_2)=1.008(1000-580)=424 \text{ kJ/kg}.$$

The quantity of rejected heat

$$q_2 = c_p(T_4 - T_1) = 1.008(518 - 300) = 220 \text{ kJ/kg}.$$

The usefully utilized heat

$$q = 424 - 220 = 204 \text{ kJ/kg}.$$

The thermal efficiency of the cycle is equal to

$$\eta_t = \frac{l}{q_1} = \frac{203}{424} = 0.482,$$

or

$$\eta_t = 1 - \frac{1}{\beta^{(k-1)/k}} = 1 - \frac{1}{10.0^{0.286}} = 0.482.$$

Example 18-2. The cycle of a constant-volume combustion gas-turbine is realized with initial parameters of the working medium $p_1 = 1$ bar and $T_1 = 300$ K. The pressure ratio of the process of adiabatic compression $\beta = p_2/p_1 = 10$ and the adiabatic exponent $k = 1.4$. The temperature at point *3* must not exceed 1000 K. The working medium is air with constant heat capacities; calculation should be reduced to 1 kg of the working medium.

Determine the parameters at the three main points, the work of expansion, compression and useful work, the quantities of added and rejected heat, the thermal efficiency of the cycle.

The initial specific volume of the working medium

$$v_1 = \frac{RT_1}{p_1} = \frac{287 \times 300}{10^5} = 0.86 \text{ m}^3/\text{kg}.$$

Parameters at point *2:*

$$p_2 = p_1 \times 10 = 10 \text{ bar};$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k}; \quad T_2 = 300 \times 10^{0.286} = 580 \text{ K};$$

$$v_2 = \frac{RT_2}{p_2} = \frac{287 \times 580}{10 \times 10^5} = 0.17 \text{ m}^3/\text{kg}.$$

Parameters at point *3:*

$$T_3 = 1000 \text{ K}; \quad v_3 = 0.17 \text{ m}^3/\text{kg};$$

$$\frac{p_3}{p_2} = \frac{T_3}{T_2}; \quad p_3 = 10\left(\frac{1000}{580}\right) = 17.25 \text{ bar}.$$

Parameters at point *4:*

$$p_4 = 1 \text{ bar};$$

$$\frac{v_4}{v_3} = \left(\frac{p_3}{p_4}\right)^{1/k}; \quad v_4 = 0.17 \times 17.25^{0.714} = 1.27 \text{ m}^3/\text{kg};$$

$$T_4 = \frac{v_4 p_4}{R} = \frac{10^5 \times 1.27}{287} = 443 \text{ K}.$$

The work of compression

$$l_1=p_1(v_4-v_1)+\frac{1}{k-1}(p_2v_2-p_1v_1)=10^5(1.27-0.86)+$$

$$+\left(\frac{10^5}{0.4}\right)(10\times0.17-0.86)=242 \text{ kJ/kg.}$$

The work of expansion

$$l_2=\frac{1}{k-1}(p_3v_3-p_4v_4)=\frac{10^5}{0.4}(17.25\times0.17-1.27)=400 \text{ kJ/kg.}$$

The useful work of the cycle

$$l=l_2-l_1=400-242=158 \text{ kJ/kg.}$$

The quantity of added heat

$$q_1=c_v(T_3-T_2)=0.72(1000-580)=302 \text{ kJ/kg.}$$

The quantity of rejected heat

$$q_2=c_p(T_4-T_1)=1.008(443-300)=144 \text{ kJ/kg.}$$

The usefully realized heat

$$q=q_1-q_2=302-114=158 \text{ kJ/kg.}$$

The thermal efficiency of the cycle

$$\eta_t=\frac{l}{q_1}=\frac{158}{302}=0.524.$$

or

$$\eta_t=1-\frac{k(\lambda^{1/k}-1)}{\beta^{(k-1)/k}(\lambda-1)}=1-\frac{1.4(1.73^{0.714}-1)}{10^{0.286}(1.73-1)}=0.52.$$

Example 18-3. Determine the temperatures at all points of the theoretical cycle realized in a constant-pressure combustion gas-turbine plant at $p=\text{const}$ and also of the cycle of a gas-turbine operated with complete heat regeneration (see Fig. 18-4); also determine the efficiencies of these cycles with given: $t_1=25$ °C; pressure ratio of the compression process in the compressor $\beta=\frac{p_2}{p_1}=5$; gas inlet temperatures at the turbine nozzles $t_3=800$ °C. The properties of the working medium are similar to those of air and its heat capacity is constant. The ideal cycle is represented by area *12341* and the cycle with complete heat regeneration—by area *1273481*.

Let us determine the temperatures at all points of the cycles

$$T_2=T_1\beta^{(k-1)/k}=298\times5^{0.286}=473 \text{ K;}$$

$$T_4=\frac{T_3-T_1}{T_2}=\frac{1073\times298}{473}=677 \text{ K.}$$

The thermal efficiency of the ideal cycle of the gas-turbine plant

$$\eta_{t\,id}^{g\text{-}t\,p}=1-\frac{q^2}{q_1}=1-\frac{T_4-T_1}{T_3-T_1}=1-\frac{677-298}{1073-473}=0.368,$$

or

$$\eta_{t\,id}^{g\text{-}t\,p}=1-\frac{1}{\beta^{(k-1)/k}}=1-\frac{1}{5^{0.286}}=0.368.$$

The thermal efficiency of a gas-turbine plant operated with complete heat regeneration

$$\eta_{t\,c\cdot r}^{g\text{-}t\,p}=\frac{l_0}{q_{1\,reg}}=\frac{(T_3-T_4)-(T_2-T_1)}{T_3-T_4}=\frac{(1073-677)-(473-298)}{1073-677}=0.558,$$

or

$$\eta_{t\,c\cdot r}^{g\text{-}t\,p}=1-\frac{T_1}{T_4}=1-\frac{298}{677}=0.558.$$

Example 18-4. Determine the thermal efficiency of the ideal cycle of a gas-turbine plant operated with heat addition at $p=\text{const}$, i.e. of a constant-pressure combustion gas turbine, and also the thermal efficiency of the real cycle, i.e. with account taken of the irreversibility of the processes of expansion and compression proceeding in the turbine and compressor, if the internal relative efficiencies of the turbine and compressor are equal to $\eta_{turb}=0.88$ and $\eta_{comb}=0.85$. The gas-turbine plant is operated at $t_1=20$ °C, the pressure ratio of the compression process in the compressor $\beta=6$; the gas inlet temperature at the turbine nozzles $t_3=900$ °C. The properties of the working medium are similar to those of air, its heat capacity is constant; the adiabatic exponent is assumed to be $k=1.4$.

Determine the temperatures at all points of the cycles

$$T_2=T_1\beta^{(k-1)/k}=293\times 6^{0.286}=488 \text{ K};$$

$$T_4=\frac{T_3T_1}{T_2}=\frac{1173\times 293}{488}=704 \text{ K}.$$

The temperature at point *5* is determined with the aid of the internal relative efficiency of the compressor:

$$T_5=\frac{T_2-T_1}{\eta_{comp}}+T_1=\frac{488-293}{0.85}+293=523 \text{ K}.$$

The temperature at point *6* is determined making use of the internal relative efficiency of the gas turbine:

$$T_6=T_3-\eta_{turb}(T_3-T_4)=1173-0.88(1173-704)=760 \text{ K}.$$

The thermal efficiency of the ideal gas-turbine cycle

$$\eta_{t\,id}^{g\text{-}t\,p}=1-\frac{T_4-T_1}{T_3-T_2}=1-\frac{704-293}{1173-488}=0.40,$$

and the thermal efficiency of the real cycle of the gas-turbine plant

$$\eta_{t\,r}^{g\text{-}t\,p}=1-\frac{T_6-T_1}{T_3-T_5}=1-\frac{760-293}{1173-523}=0.28.$$

CHAPTER NINETEEN

VAPOUR POWER CYCLES

19-1. The Carnot Cycle

Steam-turbine plants differ from internal combustion engines in that the products of combustion only serve as an intermediate heat-carrying agent, and the working medium is the vapour of some liquid, usually water vapour or steam.

In steam-turbine plants work is produced in the following way (Fig. 19-1). The chemical energy released upon fuel combustion converts into the internal energy of the products of combustion which, in the form of heat, is transferred to the water and steam generated in boiler *1* and the superheater *2*. The steam generated in the boiler is directed to steam turbine *3* where heat is converted into mechanical work, then, usually, into electric power in electric generator *4*. The waste steam passes from the turbine into condenser *5* where heat is transferred from it to the condenser cooling water. The condensate forming in the condenser is directed by the condensate removal pump *6* into feedwater tank *7*, from where feedwater is drawn by feed pump *8* that compresses feedwater to a pressure equal to boiler drum pressure. The feed pump delivers feedwater into boiler *1* through heater *9*.

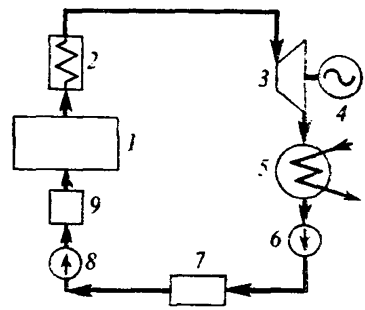


FIG. 19-1

It is well known that the most perfect ideal cycle is the Carnot cycle. The Carnot cycle associated with saturated steam is shown in Fig. 19-2. Point *O* on the *p-v* diagram characterizes the initial state of water boiling at the pressure p_1. The heat q_1 that is transferred to the boiling water at a constant temperature T_{s1} and constant pressure p_1 is equal to the heat of vaporization or latent heat r (process *0-1*). The dry saturated vapour formed expands adiabatically in the cylinder of the steam turbine from point *1* to pressure p_2 (process *1-2*). In the process of expansion steam temperature drops to condenser T_{s2} and the dryness fraction of the steam decreases

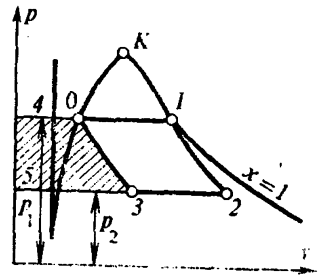


FIG. 19-2

from $x=1$ to x_2. The forming wet steam with a dryness fraction x_2 condenses partly at the constant temperature T_{s2} and pressure p_2 to point *3* (process *2-3*) with the dryness fraction of the steam decreasing to x_3. The quantity of heat transferred (rejected) from the steam is $q_2=r_2(x_2-x_3)$. From point *3* steam is compressed adiabatically in the compressor to the initial state and the entire steam turns into boiling water.

A steam-turbine plant operated on the Carnot cycle must comprise a steam boiler (process *0-1*), steam engine (turbine), process *1-2*, condenser (process *2-3*) and compressor (process *3-0*). The thermal efficiency of the Carnot cycle realized with saturated steam as the working medium is determined from the equation

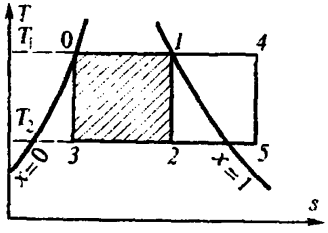


FIG. 19-3

$$\eta_t=\frac{T_{s1}-T_{s2}}{T_{s1}}=\frac{q_1-q_2}{q_1}=\frac{(i_1-i_0)-(i_2-i_3)}{i_1-i_0}.$$

The use of superheated steam to realize the Carnot cycle does not result in a higher cycle efficiency, if the temperature interval is left unchanged. In Fig. 19-3 the Carnot cycle realized with saturated steam is represented by area *01230*, and with superheated steam—by area *04530*. It is clear from the illustration that the efficiencies of the two cycles are the same.

Steam-power plants operating on the Carnot cycle have essential shortcomings that make their application inexpedient. These shortcomings are as follows: in the process *2-3* no complete condensation of steam takes place and because of this, to ensure adiabatic compression of the wet steam from point *3* to *0* a compressor with a considerable cylinder volume must be available, and this involves a great metal expenditure. The size of the compressor cylinder increases with the initial steam pressure and a decrease of condenser pressure, i.e. when passing to more advantageous temperature conditions. In addition, the fact that the Carnot cycle must be realized only in the two-phase region does not permit a high initial steam temperature, bounded by the critical temperature, i.e. makes it impossible to operate the plant with sufficiently high thermal efficiencies.

But the most important shortcoming consists in that the real work expended to drive the compressor exceeds by far the theoretical work due to the great losses in the compressor associated with the irreversibility of the processes involved. Compared with theoretical work, by 50 per cent and more, these losses may increase the real work.

19-2. The Rankine Cycle

Steam-turbine plants are usually operated on the ideal Rankine cycle. In this cycle complete condensation of the working medium takes place, so the cumbersome and inefficient compressor delivering feedwater to the boiler may be replaced by a feedpump which is small and highly efficient.

With the comparatively small power consumption of the feed pump, the losses occurring in it prove to be small compared with the overall power rating of the steam-power plant. In addition, the Rankine cycle can be realized with superheated steam which makes it possible to raise the integral mean temperature of heat addition, increasing, thereby, the thermal efficiency of the cycle.

Shown in Fig. 19-4 is the ideal Rankine cycle plotted on a *p-v* diagram. Point *4* characterizes the state of water boiling in the boiler at a pressure p_1. Line *4-5* represents the process of vaporization in the boiler; then the forming

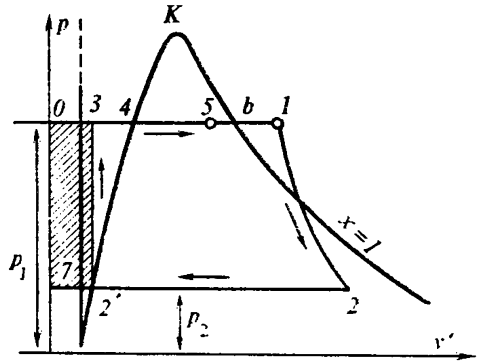


FIG. 19-4

steam is dried in a superheater—process *5-6;* process *6-1* represents superheating of the steam in the superheater at the pressure p_1. The generated steam expands adiabatically in the cylinder of a steam engine to the condenser pressure p_2. During the process *2-2'* the steam condenses completely to the state of boiling liquid at the pressure p_2, transferring the heat of vaporization to the condenser cooling water. The process of compression *2'-3* takes place in the pump, and the resulting increase in water temperature is negligibly small (in investigation carried out at pressures up to 30-40 bar this increase in temperature is ignored). Line *3-4* represents the change on the volume of water upon heating from condenser temperature to the boiling point. The work done by the feed pump is represented on the diagram by the shaded area *032'7*. The enthalpy of steam at the superheater outlet, at point *1*, is equal to i_1 and this heat is represented on the *T-s* diagram (Fig. 19-5*a*)* by area *92'34617109*. The enthalpy of steam at the inlet to the condenser at point *2* is equal to i_2 and represented on the *T-s* diagram by area *92'27109*. The enthalpy of water at the condenser outlet, point *2'*, is equal to i'_2 and represented on the *T-s* diagram by area *92'8109*. The useful work *l* done by the steam in the Rankine cycle is depicted on the *p-v* diagram by area *2'346122'* (Fig. 19-5*a*).

* When processes are plotted on the *T-s* diagram the anomality of water is neglected.

If the Rankine cycle is considered with account taken of the work done by the pump, the process of adiabatic water compression shall be represented on the *T-s* diagram (Fig. 19-5*a*) by the adiabat *2'-3*, and the isobar *3-4* corresponds to heating of the water in the boiler at the pressure p_1 to the corresponding boiling point.

The thermal efficiency of the Rankine cycle is determined by the equation

$$\eta_t = \frac{q_1 - q_2}{q_1}.$$

The amount of heat q_1 is added in the cycle at p=const during the processes *3-4* (heating of water to the boiling point), *4-6* (vaporization) and *6-1* (steam superheating), as shown in Fig. 19-5*a*.

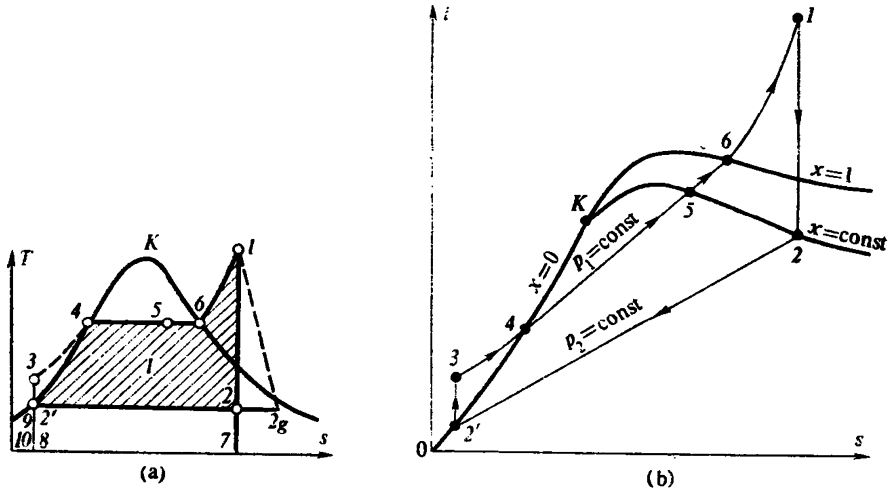


FIG. 19-5

For 1 kg of steam q_1 is equal to the difference between the enthalpies at the initial and final points of the process, i.e.

$$q_1 = i_1 - i_3.$$

This amount of heat is represented on the *T-s* diagram by area *82'346178*. Rejection of heat q_2 is effected in the condenser along the isobar *2-2'*, consequently

$$q_2 = i_2 - i_{2'}.$$

The heat rejected (transferred) from the working medium is represented on the *T-s* diagram by area *2'2782'*. The thermal efficiency of the Rankine cycle is determined by equation

$$\eta_t = \frac{(i_1 - i_2) - (i_3 - i_{2'})}{i_1 - i_3} \qquad (19\text{-}1)$$

The thermal efficiency of the Rankine cycle can also be determined from the equation

$$\eta_t = \frac{l}{q_1},$$

where l is the useful work output of the cycle.

The useful work output of the cycle is equal to the work performed by the steam turbine less the amount of work expended to drive the pump. The work done by the turbine is equal to the decrease in enthalpy during the process represented by line *1-2*

$$l_t = i_1 - i_2.$$

Adiabatic compression of water in the feed pump and in delivery to the boiler involves the expenditure of work

$$l_p = i_3 - i_{2'}.$$

Then

$$l = l_t - l_p = (i_1 - i_2) - (i_3 - i_{2'}),$$

whence the efficiency of the Rankine cycle is equal to

$$\eta_t = \frac{(i_1 - i_2) - (i_3 - i_{2'})}{(i_1 - i_3)}.$$

Taking into consideration that water is practically incompressible, Eq. (19-1) can be presented in another form.

With adiabatic compression of water in the pump and $v = \text{const}$

$$l_p = i_3 - i_{2'} = \int_{p_2}^{p_1} v\,dp = v(p_1 - p_2),$$

where v is the specific volume of water at the pressure p_2.

The work expended to drive the pump is represented on the p-v diagram by area 032'70 (Fig. 19-4).

Replacing in Eq. (19-1) the difference $(i_3 - i_2'')$ with the term $v(p_1 - p_2)$, we obtain

$$\eta_t = \frac{(i_1 - i_2) - v(p_1 - p_2)}{i_1 - i_3},$$

but

$$i_3 = i_{2'} + v(p_1 - p_2),$$

therefore

$$\eta_t = \frac{(i_1 - i_2) - v(p_1 - p_2)}{i_1 - i_{2'} - v(p_1 - p_2)}. \qquad (19\text{-}2)$$

The equation (19-2) for the thermal efficiency of the Rankine cycle is used in this form for engineering calculations.

Figure 19-5*b* presents the Rankine cycle on the *i-s* diagram. Point *1* characterizes the state of superheated steam at the inlet to the steam turbine. Point *2*—the state of wet steam at the inlet to the condenser or the state of waste steam at the turbine outlet end. Point *2'* represents the state of boiling water at the outlet from the condenser. Point *3*—the state of water at the outlet from the pump at the boiler drum pressure p_1. Point *4* characterizes the state of the boiling feedwater at the boiler drum pressure p_1, point *5*—the state of wet steam at the boiler outlet valve, and point *6* represents the state of dry saturated steam in the superheater.

On that diagram the distance between points *1* and *2* on the ordinate axis corresponds to the adiabatic expansion of steam in the steam turbine. The distance between ordinates *2* and *2'* represents the amount of heat rejected in the condenser at p_2=const. The distance between ordinate points *2'* and *3* depicts the heat expended to compress the water in the pump to boiler pressure p_1. The distance between ordinates *3* and *4* represents the amount of heat spent to heat the feedwater to boiler temperature. The distance between ordinates *4* and *5* represents the amount of heat expended to generate wet steam in the boiler with a dryness fraction x_b=const. The distance between the ordinates of points *5* and *6* and *6* and *1* determines the quantity of heat expended to dry the wet steam and superheat the dry steam in the superheater at the boiler pressure p_1=const.

Thus the quantity of heat q_1 added to 1 kg of water in the cycle is determined by the distance between ordinates *1* and *3* and the amount of heat rejected, q_2—by the distance between points *2* and *2'* plotted on the axis of ordinates.

The *i-s* diagram facilitates considerably the calculation of thermodynamic processes and cycles, since the amounts of heat are represented on the diagram by straight lines plotted on the ordinate axis between the initial and final points of the processes.

It will be recalled that when dealing with low pressures the Rankine cycle is calculated making the following assumptions: no account is taken of the rise in water temperature upon adiabatic compression in the pump (points *3* and *2'* practically merge on the *T-s* diagram); it is assumed that the isobars of the liquid merge with the liquid-phase boundary curve due to the fact that the specific volume of water is negligibly small compared with the volume of steam; the work of the pump may be ignored. Therefore, allowing for the assumptions made, the Rankine cycle acquires the graphical form illustrated in Fig. 19-6, and the thermal efficiency of the turbine vapour cycle is determined by the approximate formula

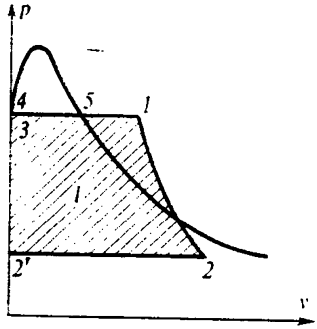


FIG. 19-6

$$\eta_t = \frac{i_1 - i_2}{i_1 - i_{2'}}. \qquad (19\text{-}3)$$

The thermal efficiency of the Rankine cycle is equal to the ratio of the adiabatic heat drop to the enthalpy of superheated steam minus the enthalpy of water at the condenser pressure. Calculation data is taken from Steam Tables or from the *i-s* diagram for steam.

When calculating steam-turbine plants and their individual component elements the mass rate of steam flow, commonly denoted by d, must be known.

The theoretical mass rate of steam flow, MJ, amounts to

$$d_{theor}=\frac{1000}{i_1-i_2},$$

where i_1 and i_2 are enthalpies, kJ/kg.

The theoretical mass rate of steam flow, d_t, expressed in kg/kW·h, is determined by the formula

$$d_t=\frac{3600}{i_1-i_2} \text{ kg/kW·h},$$

where i_1 and i_2 are expressed in kJ.

The losses due to the irreversible expansion of steam in the turbine are accounted for by the internal relative efficiency of the turbine

$$\eta_{ir}=\frac{i_1-i_{2r}}{i_1-i_2},$$

where i_{2r} is the enthalpy at the end of real expansion of steam in the turbine.

The losses due to irreversibility of processes, reduce the useful work and increase the specific steam consumption

$$d_{real}=\frac{1000}{i_1-i_{2r}}.$$

19-3. The Influence of Main Parameters on the Rankine Cycle Efficiency

Investigations of the thermal efficiency of the Rankine cycle realized at various initial and final steam conditions permit the conclusion that with an increase of the initial pressure and final temperature of steam and with a lower final condenser pressure the efficiency of steam-turbine plants increases. Let us find out how these parameters effect the efficiency of the Rankine cycle.

The influence of initial steam pressure. With an increase of the initial steam pressure and the same final pressure maintained in the condenser, the efficiency of a steam-turbine plant increases considerably and the specific rate of steam flow through the turbine, or steam consumption, diminishes.

An increase of the initial steam pressure from p_1 to p_2 is associated with an increase of the temperature of saturated steam, i.e. an increase of the

mean temperature of heat addition, which is clearly seen from the *T-s* diagram (Fig. 19-7*a*). An increase of the mean temperature at which heat is added and rejected in the condenser at $p=\text{const}$ leads to a higher cycle efficiency. Consequently, it is not the initial pressure that causes an increase of the efficiency of a steam-turbine plant, but the increase of the mean temperature of heat addition. It can also be seen from the *i-s* diagram (Fig. 19-7*b*) that an increase of the initial steam pressure causes an increase

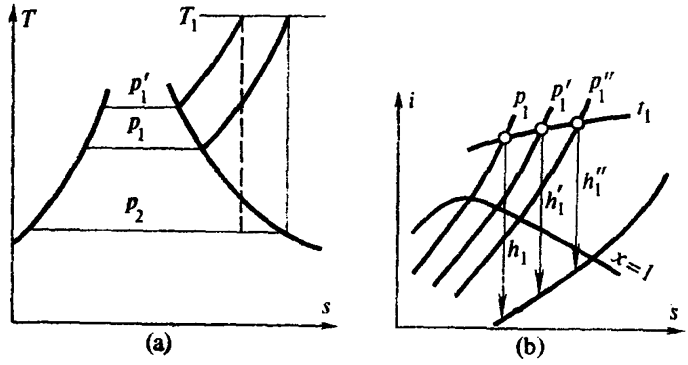


FIG. 19-7

of the adiabatic heat drop h_1, but it results in a greater final steam wetness, and water droplets destroy the blades of the last low-pressure turbine stages. A final steam wetness exceeding 13-14 per cent is inadmissible.

A considerable increase of efficiency with an increase of the initial steam pressure is of paramount importance in improving the efficiency of steam power plants. At the present time steam pressures up to 300 bar are being practised.

The influence of initial steam temperature. An increase of the initial steam temperature causes a higher efficiency of the steam-turbine cycle since this involves an increase of the integral mean temperature of heat addition associated with a greater heat drop *h* (Fig. 19-8). A more considerable rise of the cycle efficiency can be gained, if the increase of temperature is combined with an increase of the initial steam pressure. For instance, when at an initial pressure of 20 bar the temperature is raised from 400 to 550 °C the cycle efficiency increases from 0.332 to 0.355. But if, simultaneously, pressure is also increased, for instance, to 200 bar under the same conditions, cycle efficiency shall increase from 0.405 to 0.434.

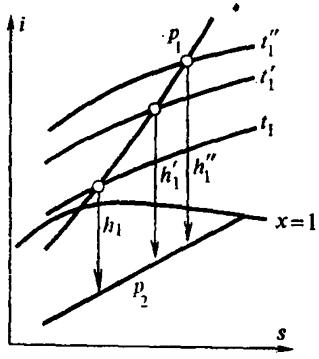


FIG. 19-8

An increase of the initial steam temperature is accompanied by a decrease in the

rate of steam flow, or specific steam consumption. Presently, turbines are operated with steam at a temperature of up to 565 °C and trial operation with steam at a temperature up to 600 °C is being carried out. The increase of steam superheating temperature is restricted by the ability of the metal from which tubes are manufactured to withstand great pressures at high temperatures, i.e. the final parameters of steam are determined by the presence of relatively cheap heat-resistant metals.

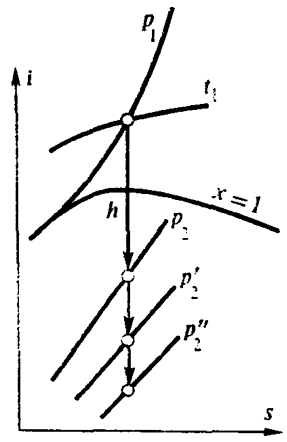


FIG. 19-9

The influence of final condenser pressure. A decrease of condenser pressure is the most effective means for increasing the thermal efficiency of a steam-turbine plant. It is clear from the *i-s* diagram shown in Fig. 19-9 that a decrease of condenser pressure reduces to a great extent the integral mean temperature of heat rejection and increases the adiabatic heat drop h and, consequently, the efficiency of the cycle. For instance, at an initial pressure of 100 bar, $t_1=600$ °C and a final (condenser) pressure of 1 bar the cycle efficiency is equal to 0.308. If condenser pressure is decreased to 0.3 bar, the cycle efficiency increases to 0.356. If condenser pressure is decreased to 0.05 bar, corresponding to a saturation temperature of 33 °C, cycle efficiency rises to 0.417. However, the selection of the final condenser pressure is determined by the temperature of the cooling water available, since intensive heat transfer from the exhaust steam to the cooling water requires that the difference in temper ture between the steam and cooling water be from 10 to 15 °C.

19-4. Reheat Cycle

Investigations of the performance of a steam-turbine plant show that an increase of the initial pressure and decrease of the final pressure lead to a higher cycle efficiency. However an increase of the initial pressure alone increase the final steam wetness.

The wetness of steam at the end of expansion is reduced by raising its initial temperature. But at a pressure of 100 bar and a temperature of 560 C° and a final condenser pressure of 0.05 bar the dryness fraction of steam in an ideal cycle is already equal to 0.79, and at a pressure of 200 bar, the dryness fraction is 0.74.

One of the methods of increasing the dryness fraction of steam at the turbine exit consists in reheating the steam. In this method superheated steam from the boiler passes at the initial pressure and temperature into the first turbine cylinder, consisting of several stages, where the steam expands adiabatically to some pressure p_1'. The steam is then extracted from the turbine and directed to flow into a special reheat superheater where it is

reheated at a constant pressure. Then the steam is again returned to the turbine where it continues to expand in turbine stages to the condenser pressure. A reheat cycle of this kind is shown in Fig. 19-10. Point *1* corresponds to the initial steam conditions; point *2*—to the final state of the steam at the turbine outlet after a second superheating; point *2'* corresponds to the final state of steam at the turbine outlet when no reheating is practised. As a result of reheating the final dryness fraction of steam increases from x_2 to x_1. In addition, reheating of steam yields some economy (2 to 3 per cent) if the mean temperature of heat addition in the reheat cycle 7-2-2'-6-7 is higher than the mean temperature of heat addition on the cycle without reheat, and the economy will be the greater the higher the temperatures at the initial and final reheat points. At pressures near to critical and supercritical two or more reheats are sometimes practised. Then the thermal efficiency of the reheat cycle is equal to

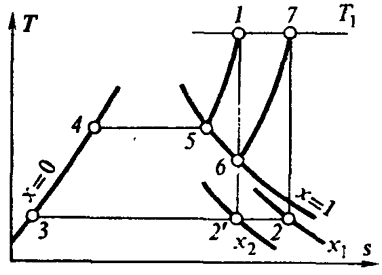


FIG. 19-10

$$\eta_t = \frac{(i_1 - i_6) + (i_7 - i_2)}{(i_1 - i_3) + (i_7 - i_6)}, \tag{19-4}$$

where $(i_1 - i_6)$ and $(i_7 - i_2)$ = adiabatic heat (or enthalpy) drops in the first and second turbine cylinders;

$(i_1 - i_3)$ = quantity of heat added in the boiler and (first) superheater;

$(i_7 - i_6)$ = quantity of heat added in the reheater.

The mass rate of steam flow through the turbine, measured in units of kg/MJ, is equal to

$$d = \frac{1000}{(i_1 - i_6) + (i_7 - i_2)}. \tag{19-5}$$

19-5. Regenerative Cycle of a Steam-Turbine Plant

It is commonly known that the thermal efficiency of a cycle can be raised considerably by introducing heat regeneration.

A conventional maximum-regenerative cycle of a steam-turbine plant is represented in Fig. 19-11. In this cycle feedwater is heated at the expense of the heat rejected in the process represented by line *2-3*, with the quantity of heat removed in the process *2-3* and measured by area *27832* being equal to the amount of heat added in the process *4-5* and measured by area *04590*. Equality of the areas is possible only when the curves *4-5* and *2-3* are equidistant. Since the mean temperature at which heat is added to the working medium from an external source is higher than the heat addition

temperature in the ordinary Rankine cycle, the regenerative cycle has a higher efficiency that is still lower than that of a Carnot cycle realized in the same temperature interval.

A study of the cycle shown in Fig. 19-11 leads to the conclusion that the heat used along line *2-3* to heat water in the process *4-5* diminishes the specific useful work done by the steam in a regenerative cycle, compared with the work performed in the ordinary cycle, i.e. that the regenerative cycle is characterized by a greater specific steam consumption.

Because of the equality of the areas below the curves of processes *2-3* and *4-5*, the cycle depicted in Fig. 19-11 can be replaced with a cycle equivalent with respect to thermal efficiency, shown in Fig. (19-12). The thermal efficiency of such a cycle

$$\eta_t = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2(s_1 - s_1')}{i_1 - i_1'},$$

where T_2 = absolute steam temperature in condenser;
s_1 = entropy of superheated steam;
s_1' = entropy of liquid boiling at initial pressure;
i_1 = enthalpy of superheated steam;
i_1' = enthalpy of liquid boiling at initial pressure p_1.

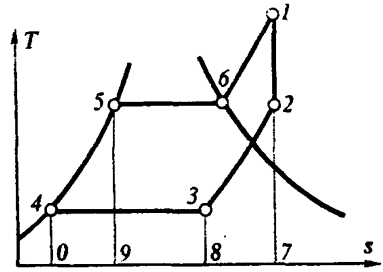


FIG. 19-11

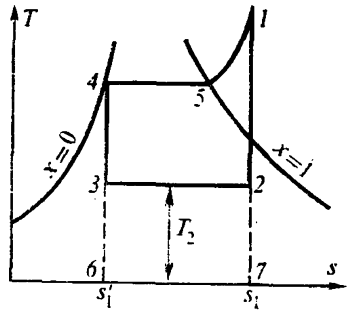


FIG. 19-12

The above formula can be used to calculate the thermal efficiency of a steam-turbine plant operated on a maximum-regenerative cycle.

In practice, regenerative feedwater heating is effected in several series connected heaters to each of which a small quantity of steam enters, extracted from the corresponding turbine stage. When this method of steam extraction is practised a gradually diminishing quantity of steam flows through the individual turbine stages, with the greatest fraction of the steam, which takes no part in feedwater heating, expanding to the pressure maintained in the condenser just as in the Rankine cycle.

It is impossible to give a direct representation of the regenerative cycle of a steam-turbine plant on thermodynamic diagrams of state, since, following each extraction, the quantity of steam changes from stage to stage. Depending on the way in which the heating steam and heater condensate are connected to the common feedwater system, various regenerative feedwater heating arrangements are possible, differing from one another in attendance and economical characteristics.

Shown in Fig. 19-13 is the arrangement of feedwater heating in a steam-power plant featuring three steam bleedings and cascade-draining of bleed-steam condensate. The following notations are used in the illustration: *1*—steam boiler; *2*—steam superheater; *3*—steam turbine; *4*—condenser; *5*—feedwater pump; *6*—surface heater; *7*—bleed-steam condensate pump; *8*—bleed-steam condensate; *9*—feedwater; *10*—heating bleed steam from a turbine stage. From boiler *1* steam flows to turbine *3* at pressure p_1, temperature t_1 and its enthalpy i_1; in condenser *4* steam pressure is p_2,

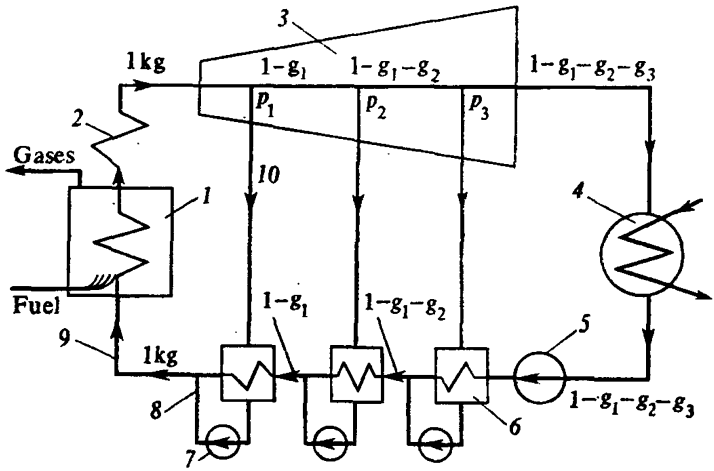


FIG. 19-13

temperature t_2 and enthalpy i_2. Not all the steam flows through the turbine. Of each kilogram of steam passing to the turbine the following amounts are bled back: g_1 kg into the first heater *6* with an enthalpy i', pressure p' and temperature t'; g_2 kg into the second heater with an enthalpy i'', pressure p'' and temperature t''; g_3 kg into the third heater with an enthalpy i''', pressure p''' and temperature t'''; g kg of bleed-steam condensate is drained off.

Then

$$g_1+g_2+g_3+g=1$$

The condensate forming after the turbine at a pressure p_2 and temperature t_2 is delivered by condensate pump *5* through the three regenerative feedwater heaters *6* in succession, and after being heated in them to a temperature higher than that of the water in the condenser, feedwater is delivered by feed pump *5* into the boiler. The temperature of feedwater is t' and enthalpy t_{fw}. The useful work done by 1 kg of steam in an ideal turbine operated with regenerative feedwater heating is less than i_1-i_2, the work

done by the steam in the cycle, l, is determined as the sum of the work done by the flows of steam passing through the turbine

$$l=l_1+l_2+l_3+l_4.$$

The thermal efficiency of the regenerative cycle is equal to

$$\eta_t=\frac{q_1-q_2}{q_1}=\frac{l}{q_1},$$

where q_1 = amount of heat, equal to the difference i_1-i_{fw};
i_{fw} = enthalpy of feedwater at temperature t', equal to the saturation temperature at the pressure p' at the first bleed point.

Upstream from the first bleed point 1 kg of steam passes through the turbine, therefore

$$l_1=i_1-i'.$$

Between the first and second bleed points an amount of steam $(1-g_1)$ expands performing the following work

$$l_2=(1-g_1)(i'-i'').$$

Between the second and third bleed points $(1-g_1-g_2)$ kg of steam expands. The work done by the steam is equal to

$$l_3=(1-g_1-g_2)(i''-i''').$$

Between the third bleed point and the condenser the expanding steam performs the following amount of work

$$l_4=(1-g_1-g_2-g_3)(i'''-i_2)$$

The work output of the turbine is determined as the work done by the steam in all turbine stages

$$l=(i_1-i')+(1-g_1)(i'-i'')+(1-g_1-g_2)(i''-i''')+$$
$$+(1-g_1-g_2-g_3)(i'''-i_2),$$

or

$$l=i_1-i'g_1-i''g_2-i'''g_3-i_2g.$$

The thermal efficiency of the regenerative cycle is equal to

$$\eta_t=\frac{l}{q}=\frac{(i_1-i'g_1-i''g_2-i'''g_3-i_2g)}{i_1-i_{fw}} \tag{19-6}$$

Steam consumption in kilograms per 1 MJ is

$$d=\frac{1000}{l}=\frac{1000}{i_1-i'g_1-i''g_2-i'''g_3-i_2g} \tag{19-7}$$

It is most convenient to determine the enthalpy of steam at the bleed points on the i-s diagram shown in Fig. 19-14. Using the data on the given

initial state of the steam conditions at the turbine throttle and the final state of the steam in the condenser, we draw the adiabat of expansion. Projecting onto the axis of coordinates the state of intermediate points at the steam bleed points, we determine the corresponding values of the enthalpies. The rates of steam flow at the bleed points are determined from the heat balance equations written for the regenerative feedwater heaters, assuming that the temperature of feedwater and bleed-steam condensate in each of the heaters is equal to the saturation temperature of the steam passing through it. For instance, into the first heater an amount $(1-g_1)$ kg of water with an enthalpy i_0'' flows from the second heater together with g_1 kg of bleed steam and also bleed steam in the amount of g_1 kg with an enthalpy i', while from the heater flows 1 kg of feedwater with an enthalpy i_{fw}. Then the heat balance equation for the first heater is

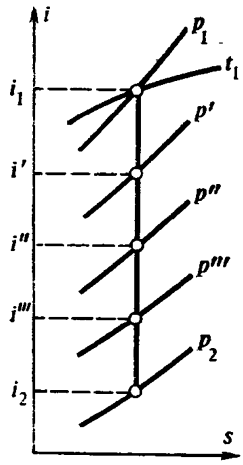


FIG. 19-14

$$i_{fw}=g_1 i'+(1-g_1)i_0''$$

whence

$$g_1=\frac{i_{fw}-i_0''}{i'-i_0''}. \qquad (19\text{-}8)$$

In a similar manner we can determine the amount of steam extracted from the turbine at any of the bleed points.

Regenerative feedwater heating increases the thermal efficiency of a steam-turbine plant by from 10 to 14 per cent, and the higher the initial steam parameters the greater the saving economy. The use of regenerative feedwater heating reduces the passages between turbine blades in the last stage and, consequently, makes it possible to decrease the size of the turbine.

Regenerative feedwater heating diminishes the irreversibility of the process of transferring heat in the boiler from the hot gases to the working medium, since the average temperature of the working medium increases with rising initial temperature and this in its turn diminishes the difference between the temperatures of the hot gases (combustion products) and the working medium.

19-6. Binary Cycles

Water, used as the working medium in a vapour cycle, has an essential shortcoming in that the critical pressure of water is high (221.15 bar) at a comparatively low critical temperature ($t_{cr}=374.15$ °C).

As a result, to increase the thermal efficiency of a vapour cycle, it is necessary in conjunction with a high initial pressure to raise the initial steam temperature and this is limited by the presently available heat-resistant metals.

In addition, the need for a higher steam superheat leads to a relative decrease of the thermal efficiency of the Rankine cycle, compared with the Carnot cycle realized in the same temperature interval, since in the superheated steam region heat is added isobarically which is less effective than isothermal heat addition.

The efficiency of the Rankine cycle could be increased, if we succeeded in finding a working medium with a considerably higher critical temperature than that of water at a moderate critical pressure. Then the process of heat addition could be realized at higher temperatures in the saturated vapour region without any subsequent superheating, i.e. in an isothermal process at low initial pressures. The saturation temperatures of such a working medium should not be too low in the low-temperature region.

Unfortunately, at the present time no working medium is known that would meet all these requirements. Therefore the idea has been conceived of creating a complex cycle with two working media, the so-called *binary cycle*, in which one of the working media must have a high critical temperature at a comparatively low pressure. This working medium is made use of in the part of the cycle realized in the high-temperature region. The other working medium must have a comparatively high saturation pressure at the temperature of the surrounding medium. This second working medium is used in the part of the cycle realized in the low-temperature region. The combination of the two cycles makes it possible to increase considerably the overall temperature drop and thereby increase the overall thermal efficiency compared with the vapour power cycle.

Used as the first working medium is mercury whose high saturation temperatures correspond to comparatively low pressures. For instance, at the temperature of saturated mercury vapour, $t_s = 582.4$ °C, the pressure is equal to 20.23 bar. The critical temperature of mercury is equal to 1420 °C. In the low-temperature region, on the lower isobar of the cycle, the more suitable working medium is water.

The schematic diagram of a power plant operated on the binary mercury-vapour cycle is shown in Fig. 19-15. The solid lines represent the mercury circuit of the binary cycle. The mercury vapour forming in mercury boiler *1* flows to the mercury turbine *3*. From the turbine the expanded mercury vapour flows into condenser-evaporator *2* where the vapour condenses and the heat of condensation is transferred to water for the purpose of steam generation. Therefore the condenser-evaporator serves simultaneously as a steam boiler. Liquid mercury usually returns by gravity into the mercury boiler, and the forming steam is directed to superheater *4* and further to

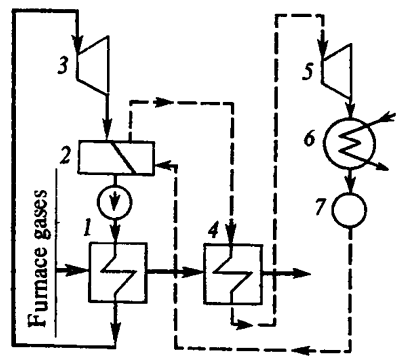


FIG. 19-15

steam turbine *5* where it produces useful work on the turbine blades. The waste steam passes into condenser *6*, then pump *7* delivers the condensate to the condenser-evaporator. The dotted lines show the water circuit of the binary cycle.

Shown in Fig. 19-16 is the *T-s* diagram of the binary mercury-water cycle. Since the enthalpy of the waste mercury vapour is several times smaller than the enthalpy of water vapour (steam), the rate of mercury vapour flow through the condenser-evaporator must be 10-12 times greater than the rate of steam flow through it. In this connection, on the *T-s* diagram, the cycle *1-2-3-4-5-1* is drawn for 1 kg of steam (water vapour) and the cycle *8-7-6-9-8*—for m kg of mercury vapour. The cycles are arranged so that the process of adiabatic mercury expansion passes on top of point *5* of dry saturated steam.

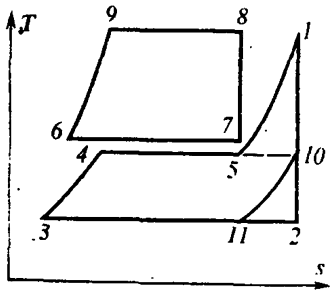


FIG. 19-16

Power plants operating on the binary cycle use dry saturated mercury vapour at pressures within 10-15 bar at temperatures from 517 to 557 °C. The admissible adiabatic expansion of the working medium in a mercury vapour turbine is to a pressure from 0.1 to 0.04 bar which corresponds to a temperature of 247 to 227 °C. The initial temperature of steam is usually 10 to 15 °C lower than the temperature of mercury vapour in the condenser (of the order of 237-217 °C), corresponding to a pressure of 33-25 bar.

To raise the efficiency of power plants operated on the binary cycle, it is advisable to use regenerative feedwater heating (process 10-11). Since the heat capacity of liquid mercury is very small, regenerative heating of liquid mercury is not effective and it is therefore not applied. Steam superheating is used to reduce the final wetness of steam upon expansion in the turbine.

The real effectiveness of the binary cycle is much higher than that of a steam power plant; the thermal efficiency of the cycle reaches from 0.8 to 0.85 of the efficiency of the Carnot cycle realized in the same temperature interval. At an initial mercury vapour temperature of 500 K and a final temperature in the water condenser equal to 30 °C the thermal efficiency of a binary cycle with regenerative feedwater heating is equal to $\eta_t = 0.57$. When mercury vapour is used at a temperature from 500 to 600 °C the efficiency of the binary cycle is still higher.

The thermal efficiency of a binary mercury-water cycle realized without regenerative feedwater heating is determined from the equation

$$\eta_t = \frac{L}{Q_1} = \frac{L_m + l_w}{Q_1} = \frac{m(i_8^m - i_7^m) + (i_1^w + i_2^w)}{m(i_8^m - i_6^m) + (i_1^w - i_5^w)}, \qquad (19\text{-}9)$$

where L_m = work done by 1 kg of mercury vapour;
l_w = work done by 1 kg of water vapour (steam);

m = rate of mercury circulation (mass of mercury per 1 kg of water in the mercury-water cycle);
i_8^m = enthalpy of mercury vapour after the mercury boiler;
i_7^m = enthalpy of mercury vapour at the exit of the mercury turbine;
i_1^w = enthalpy of superheated steam at the superheater exit;
i_2^w = enthalpy of steam at the steam turbine exhaust end;
i_6^m = enthalpy of mercury after the condenser;
i_5^w = enthalpy of saturated steam at the boiler exit.

The rate of mercury circulation, m, is found from the heat balance equation for the condenser-evaporator

$$m=(i_5^w-i_3^w)/(i_7^m-i_6^m), \tag{19-10}$$

where i_3^w is the enthalpy of water after the condenser.

The first steam power plant operated on the binary mercury-water cycle rated at 1800 kW was constructed in 1923. During the ensuing years higher capacity of mercury turbines have been constructed and at the present time turbines of 20 000 kW-power are available. The operation of power plants using the binary mercury-water cycle has shown them to be safe and reliable due to the use of high-quality welding techniques. Also their efficiency is high.

At the present time investigations are being conducted to replace mercury by cheaper substances with a higher boiling point and to create more improved cycles for the temperature interval already utilized.

19-7. The Fundamentals of Process-Steam and District-Heating Systems

It has already been shown above that under the most favourable conditions the thermal efficiency of the Rankine cycle does not exceed 50 per cent, and if account is taken of the heat losses suffered in boiler rooms upon fuel combustion, in pipelines, losses of heat due to friction in turbo-generators, then the real efficiency of a condensing steam power plant will not exceed 30 to 35 per cent. The greatest heat loss is in the condenser. The water used to ensure steam condensation has a low final temperature making its further use impracticable. This heat q_2 is represented in Fig. 19-17 by area *15761*. But if the final pressure p_2 is raised to 1-2 bar, the exhausted steam from the turbine can be used for public utility purposes (in bath houses, heating of buildings, hot water supply, etc.). If the final pressure is raised to 1.5-5.0 bar, the waste steam can be used directly for processing purposes in factories and plants. In both cases the heat of combustion of the fuel is first used to generate

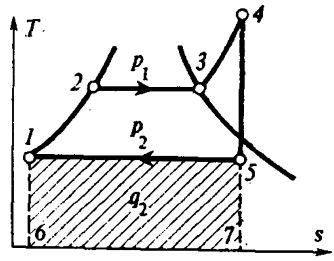


FIG. 19-17

electric power, then in multi-purpose heating appliances. Such combined production of electric power and heat for district-heating systems and processing purposes is effected with the aid of extraction and back-pressure turbines and the electric stations are referred to as *heat-and-power stations.*

The basic heat diagram of a heat-and-power station is shown in Fig. 19-18. The power station comprises steam boiler *1* with superheater *2*, steam turbine *3* with back-pressure (p_2), generating electric power, heat consumers *4* and pump *5*. There is no condenser in a plant of this kind. The magnitude of the back pressure p_2 is determined by processing and district-heating conditions. The higher the pressure p_2 the less mechanical work is done and the lower the thermal efficiency of the cycle

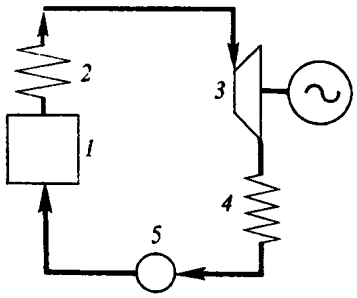


FIG. 19-18

$$\eta_t=(q_1-q_2)/q_1=l/q_1,$$

but the degree of heat utilization in the plant increases:

$$K=(l+q_2)/q_1, \qquad (19\text{-}11)$$

where l = amount of heat converted into work;
q_2 = amount of heat used by the heat consumers.

Heat-and-power stations are usually fitted with condensing extraction turbines in which heat is extracted at pressures meeting processing and district-heating (hot-water supply) requirements as well as wide ranging power supply requirements.

The development of district heating is of great importance in national economy of the USSR. The combined production of heat and electric power reduces considerably fuel consumption, compared with separate production of heat and generation of electric power. The overall coefficient of utilization of the heat of fuel in heat-and-power stations reaches 80 per cent and more. In the development of processing and district-heating systems the USSR leads in the world.

19-8. Internal Relative Efficiency of a Steam Turbine

When considering the Rankine cycle it was assumed that it consists only of reversible processes. Each of the component processes of a real cycle realized in a steam power plant is to some extent irreversible, therefore the efficiency of a real plant will be lower than the thermal efficiency of a reversible cycle.

The process *2'-3* (Fig. 19-19) is irreversible because of the loss of heat due to friction, and the processes *3-4*, *4-5*, *5-1* and *2-2'* are irreversible due to the fact that heat exchange takes place at a finite temperature difference, but the degree of irreversibility of all these processes is relatively small and,

as a first approximation, it can be ignored. The main irreversibility in a steam (turbine) power plant is associated with the loss of the kinetic energy of steam due to friction as the steam expands in the nozzles and blades of the turbine, inasmuch as steam flows through the blading with a high velocity.

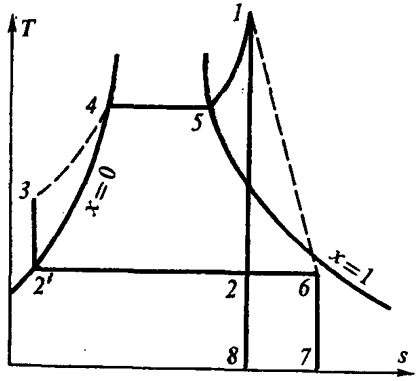


FIG. 19-19

The irreversible process of expansion *1-6* can be represented conventionally on the thermodynamic diagram of state, if its initial and final parameters are known. The useful work done by a flow undergoing an irreversible adiabatic process does not depend on the path of the process and is equal to the difference between the real enthalpies of the steam at the beginning and end of the process:

$$l_{real}=i_1-i_6.$$

Since in the irreversible process *1-6* entropy always increases, the entropy at point *6* must be greater than that at point *2*. The frictional heat that failed to convert into work serves to raise the enthalpy of steam, therefore area *2678* shall represent, or measure, the heat added to the waste steam due to the irreversibility of the process. The difference between the theoretical and real work (area *2678*) will be expressed by the equation

$$l_t-l_{real}=(i_1-i_2)-(i_1-i_6)=i_6-i_2.$$

The ratio of the real work done by the steam flow in the turbine to the theoretical work is called the *internal relative efficiency* of a steam turbine and is denoted by η_{ir}

$$\eta_{ir}=\frac{l_{real}}{l_t}=\frac{i_1-i_6}{i_1-i_2}=1-\frac{i_6-i_2}{i_1-i_2}=\frac{\text{area } 122'3451-\text{area } 26782}{\text{area } 122'3451}. \qquad (19\text{-}12)$$

19-9. Effective Efficiency of a Steam Turbine

In analyzing the performance of a steam power plant all processes are usually considered with the working medium in continuous flow through individual component elements of the plant.

The irreversibility of the processes proceeding in a steam power plant lead to a loss of work and correspondingly to a decrease in the useful work output of the plant.

The specific useful work of a steam power plant can be determined with the aid of formula (9-43), according to which

$$l_{use}=l_{max}-T_0\Delta s,$$

where l_{max} = maximum useful work (initial availability), that can be done by 1 kg of the working medium upon a change of its state from the given state to the state of the surroundings at a temperature T_0;

Δs = increase in the entropy of the system due to the irreversibility of the process.

The cycle of a steam power plant consists of successively proceeding processes represented graphically in Fig. 19-20. It can be assumed that at point *2'* the working body possesses zero availability, since its state is close to the state of the surrounding medium. Then the loss of availability in real processes will be equal to the sum of the losses of availability in individual processes.

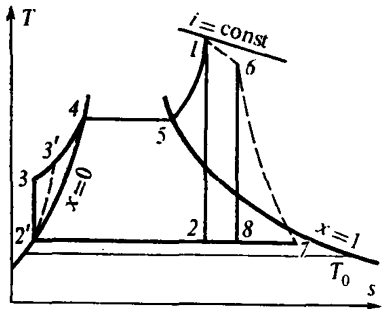


FIG. 19-20

In the general form the equation reduces into

$$l_{use}=l_{max}-\sum\Delta sT_0, \qquad (19\text{-}13)$$

where $\sum\Delta s$ is the summary increase of system entropy per 1 cycle.

The useful work input of a cycle (without account taken of the mechanical losses on the turbine shaft and transfer gear) is equal to the maximum availability of the system calculated for 1 cycle, less the total loss of availability.

If we assume that in a real steam power plant only the processes of steam expansion in the turbine blading and the process of compression are irreversible, then the useful (internal) work done by the plant can be found from the following equation:

$$l_{use}=(i_6-i_8)\eta_{ir}-(i_3-i_{2'})/\eta_{rp} \qquad (19\text{-}14)$$

where η_{ir} and η_{pr} are the internal relative efficiencies of the steam turbine and feedwater pump.

In determining the amount of heat added in a steam-turbine plant it is necessary to take into account that in the absence of losses to the surroundings the work expended in the pump to effect compression and deliver feedwater to the boiler is fully transferred to the water in the form of heat due to the irreversibility of the process of compression proceeding in the feed

pump. Therefore the amount of heat q' added from external sources is determined by formula

$$q'=(i_1-i_{2'})-(i_3-i_{2'})/\eta_{r\,p}.$$

Consequently, the internal relative efficiency of a steam-turbine plant (with no allowances made for the mechanical losses on the turbine shaft and in the transfer gear) is equal to

$$\eta_{r\,pl}=\frac{l_{use}}{q'}=\frac{(i_8-i_8)\eta_{i\,r}-(i_3-i_{2'})/\eta_{r\,p}}{(i_1-i_{2'})-(i_3-i_{2'})/\eta_{r\,p}}=\frac{(i_8-i_8)-(i_{3'}-i_{2'})}{i_1-i_{2'}} \tag{19-15}$$

The effective efficiency of a steam-turbine plant without heat regeneration and extraction of heat for processing and district-heating purposes is determined in the following way:

$$\eta_e=\frac{l_{use}}{q'}\eta_{b\,p}=\eta_b\frac{\eta_{i\,r}(i_8-i_8)-(i_3-i_{2'})/\eta_{r\,p}}{i-i_{2'}-(i_3-i_{2'})/\eta_{r\,p}}, \tag{19-16}$$

where $\eta_{b\,p}$ = the efficiency of a boiler plant;

$$\eta_{r\,p}=\frac{i_3-i_{2'}}{i_{3'}-i_{2'}}. \tag{19-17}$$

Typical Questions and Examples to Chapter Nineteen

1. What distinguishes a steam (turbine) power plant from internal combustion engines?
2. Describe the Carnot cycle for saturated steam.
3. What is the difference between the Rankine and Carnot cycles?
4. Represent the Rankine cycle on *p-v* and *T-s* diagrams.
5. How are the thermal efficiency and the specific rate of fuel flow (consumption) in the Rankine cycle determined?
6. How does the initial steam pressure influence the thermal efficiency of the Rankine cycle?
7. How does the initial steam temperature influence the thermal efficiency of the Rankine cycle?
8. How does the final pressure influence the thermal efficiency of the Rankine cycle?
9. Describe the reheat cycle of a steam power plant.
10. Describe the regenerative cycle of a steam power plant.
11. Describe the binary (mercury-water) cycle.
12. Draw the *T-s* diagram of the binary cycle.
13. What is the advantage of combined generation of electric power and heat for processing and district-heating purposes?
14. Draw the heat flow diagram of a heat-and-power station.
15. The cofficient of heat utilization for a heat-and-power station.
16. What is the importance of district heating systems for the national economy of the USSR?

17. What is meant by the internal relative efficiency of a steam turbine and how is it determined?
18. How is the specific useful work of a turbine determined?
19. What irreversible cycles compose the real cycle of a steam-turbine power plant?
20. How is the internal relative efficiency of the pump and of the steam-turbine plant determined?
21. How is the effective (thermal) efficiency of a steam-turbine plant determined?

Example 19-1. Determine the efficiency of an ideal Rankine cycle realized at an initial steam temperature $t=500$ °C and a final pressure $p_2=0.1$ bar. Solve the problem assuming: (1) initial pressure $p_1=20$ bar; (2) $p_1=50$ bar; and (3) $p_1=100$ bar.

The thermal efficiency of the ideal Rankine cycle

$$\eta_t=\frac{i_1-i_2}{i_1-i_{2'}}.$$

All the enthalpies of the steam are taken from Steam Tables.

1. $i_1=3470$ kJ/kg; $i_2=2360$ kJ/kg; $i_{2'}=192$ kJ/kg;

$$\eta_t=\frac{3470-2360}{3470-192}=0.34.$$

2. $i_1=3440$ kJ/kg; $i_2=2210$ kJ/kg;

$$\eta_t=\frac{3440-2210}{3440-192}=0.38.$$

3. $i_1=3380$ kJ/kg; $i_2=2100$ kJ/kg;

$$\eta_t=\frac{3380-2100}{3380-192}=0.402.$$

With an increase in the initial pressure the thermal efficiency of the Rankine cycle rises.

Example 19-2. Determine the thermal efficiency of a Rankine cycle realized at an initial steam pressure $p_1=40$ bar and an initial temperature $t=500$ °C. Solve the problem assuming final pressures $p_2=2$ bar; $p_2=0.5$ bar; and $p_2=0.05$ bar.

The thermal efficiency of the Rankine cycle is equal to

$$\eta_t=\frac{i_1-i_2}{i_1-i_{2'}}.$$

1. $i_1=3450$ kJ/kg; $i_2=2700$ kJ/kg; $i_{2'}=505$ kJ/kg;

$$\eta_t=\frac{3450-2700}{3450-505}=0.255.$$

2. $i_1=3450$ kJ/kg; $i_2=2470$ kJ/kg; $i_{2'}=340$ kJ/kg;

$$\eta_t=\frac{3450-2470}{3450-340}=0.315.$$

3. $i_1=3450$ kJ/kg; $i_2=2170$ kJ/kg; $i_{2'}=138$ kJ/kg;

$$\eta_t=\frac{3450-2170}{3450-138}=0.387.$$

With decreasing final pressure and the same initial steam conditions the thermal efficiency of the Rankine cycle increases.

Example 19-3. A steam-turbine plant is operated on the Rankine cycle with superheated steam at initial conditions $p_1=20$ bar, $t_1=400$ °C and a final pressure $p_2=0.05$ bar. Determine the thermal efficiency of the cycle and the specific rate of steam flow.

On the *i-s* diagram we find that $i_1=3250$ kJ/kg; $i_2=2180$ kJ/kg, $x_2=0.84$; and $i_1'=138$ kJ/kg.

The thermal efficiency of the Rankine cycle is equal to

$$\eta_t=\frac{3250-2180}{3250-138}=0.344.$$

Steam consumption per 1 MJ

$$d=\frac{1000}{i_1-i_2}=0.93 \text{ kg/MJ}.$$

If the turbine is operated with dry saturated steam, then $i_1=2800$ kJ/kg; $i_2=1940$ kJ/kg; and $i_2'=138$ kJ/kg.

The efficiency of the cycle will be

$$\eta_t=\frac{2800-1940}{2800-138}=0.323.$$

The consumption of steam per 1 MJ will be

$$d=\frac{1000}{i_1-i_2}=1.16 \text{ kg/MJ}.$$

Example 19-4. Determine the internal relative and effective efficiencies of a steam-turbine plant and the state of steam at the turbine exhaust end, if the initial steam conditions are $p_1=160$ bar, $t_1=550$ °C; condenser pressure $p_2=0.05$ bar; the internal relative efficiency of the turbine and feed pump are respectively $\eta_{rt}=0.88$ and $\eta_{rp}=0.9$; the efficiency of the boiler room $\eta_b=0.85$. The steam-turbine plant operates on the cycle shown in Fig. 19-20.

The initial enthalpy of steam at the end of adiabatic expansion is determined by the formulae.

$$s_6=s_8; \quad s_6=s_8'+\frac{r_8}{T_8}x_8; \quad 6.5=0.4764+\frac{2423.1}{306}x_8,$$

whence $x_8=0.76$.

$$i_8=i_8'+r_8x_8=137.79+2423.1\times0.76=1979 \text{ kJ/kg}.$$

The theoretical adiabatic pressure drop is equal to

$i_6 - i_8 = 3450 - 1979 = 1471$ kJ/kg.

With account taken of the internal relative efficiency of the turbine, the real pressure drop through the turbine is

$$\eta_{r\,t} = \frac{i_6 - i_7}{i_6 - i_8}; \quad i_6 - i_7 = \eta_{r\,t}(i_6 - i_8),$$

whence

$$i_7 = i_6 - \eta_{r\,t}(i_6 - i_8) = 3450 - 0.88 \times 1471 = 2156 \text{ kJ/kg}.$$

Knowing the enthalpy of steam at point *7*, we find the other parameters

$$x_7 = \frac{i_7 - i'_7}{r_7} = \frac{2156 - 137.79}{2423} = 0.83;$$

$$v_7 = v'' x_7 = 28.24 \times 0.83 = 23.4 \text{ m}^3/\text{kg},$$

where v'' is the volume of dry saturated steam at $p_2 = 0.05$ bar.

$$s_7 = s'_7 + \left(\frac{r_7}{T_7}\right) x_7 = 0.4764 + \frac{2423.1}{306} \times 0.83 = 7.05 \text{ kJ/kg·deg}.$$

The internal relative efficiency of the cycle is determined by formula

$$\eta_{r\,pl} = \frac{(i_6 - i_8)\eta_{r\,t} - (i_3 - i_{2'})/\eta_{r\,p}}{(i_6 - i_{2'}) - (i_3 - i_{2'})/\eta_{r\,p}} = \frac{(3450 - 1979)0.88 - (i_3 - 137.79)/0.9}{(3450 - 137.79) - (i_3 - 137.79)/0.9}.$$

The enthalpy and entropy of water at point *2* we find on the line of boiling liquid ($x = 0$)

$i_{2'} = i_{7'} = 137.79$ kJ/kg;

$s_{2'} = s_{7'} = 0.4764$ kJ/kg·deg.

The enthalpy of water after compression in the pump is found from the condition that the process *2-3* is adiabatic. At the pressure $p_3 = p_1 = 160$ bar and entropy $s_3 = s_{2'} = 0.4764$ kJ/kg·deg, we find from Steam tables that $i_3 = 152.8$ kJ/kg. The difference $i_3 - i_{2'} = 152.8 - 137.79 = 15.0$ kJ/kg represents the theoretical work of the pump, whence $\eta_{i\,pl} = 0.389$.

Ignoring the losses, the thermal efficiency of the Rankine cycle

$$\eta_t = \frac{(i_6 - i_8) - (i_3 - i_{2'})}{(i_1 - i_3)} = \frac{[(3450 - 1979) - 15]}{(3450 - 152.8)} = 0.451.$$

Without account taken of the work done by the pump the thermal efficiency of the Rankine cycle

$$\eta_t = \frac{i_6 - i_8}{i_6 - i_{2'}} = \frac{1471}{3212} = 0.458.$$

CHAPTER TWENTY

CYCLES OF ATOMIC POWER PLANTS, VAPOUR-GAS PLANTS AND MHD INSTALLATIONS

20-1. Thermodynamic Cycles of Atomic Power Plants

In the years following the World War II, in the Soviet Union, USA, England and other countries, atomic power plants were designed and constructed. In these use is made of the energy released when the nuclei of the heavy element isotopes uranium U^{235} and plutonium Pu^{239} are split.

The world's first atomic power plant, rated at 5000 kW, was constructed in the USSR in 1954. The investigations and studies conducted at this atomic power plant have served as the basis for the creation of improved high-capacity atomic power plants. In 1959 the world's most powerful ice breaker "Lenin" was built. Atomic power plants have also found wide application in submarines.

In operating atomic power plants the removal of the enormous quantity of heat liberated in the reactor or pile presents many difficulties. At the present time many cooling systems are known and used, but they are all built on the same principle, heat is removed by means of a circulating coolant, gas or liquid.

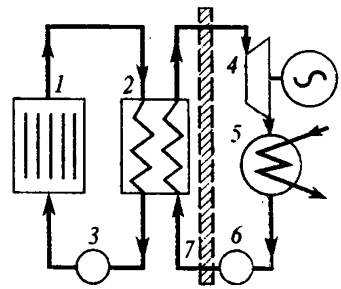


FIG. 20-1

The schematic diagram of a two-circuit atomic power plant is shown in Fig. 20-1. The fission of the nuclei of heavy elements taking place in reactor *1* is accompanied by the liberation of a great amount of heat, which is removed by a special coolant. Water, liquid metals (sodium, potassium), organic compounds and gases (carbon dioxide, helium and others) are used as coolants. The coolant which is exposed to the highly radioactive fuel elements acquires radioactivity itself. It is not directed to a turbine, but into an intermediate heat exchanger—steam generator *2* where the coolant transfers heat to the working medium of the second circuit of the steam power plant. Then pump *3* returns the coolant into the reactor again. Because of its high radioactivity, the equipment in the first circuit is separated from the remaining part of the power plant by special biological shielding *7*. The second circuit carries circulating water and steam. The steam forms in the steam generator which receives heat from the reactor coolant, and flows to turbo-generator *4* where it produces electric power. From the turbine the exhaust steam passes to condenser *5* where it condenses, and

feed pump *6* delivers the condensate as feedwater to steam generator *2*. As a coolant, water has a big drawback. It makes it impossible to generate steam in the second circuit at high pressures and temperatures. For instance, when water is used as a coolant at a pressure of 100 bar and a temperature of 320 °C, the working medium of the second circuit will be dry saturated steam at a pressure of 30 bar, and a temperature of 232 °C. When the temperature of the second-circuit working medium is as low as this the thermal efficiency of the Rankine cycle is equal to 35 per cent and, allowing for losses, the real efficiency is only 17-20 per cent. Steam at a higher pressure can be generated in the second circuit only by using another coolant with a higher boiling point at low pressures.

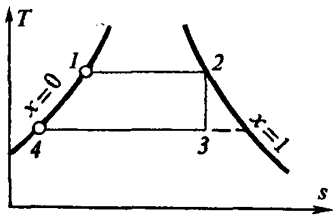


FIG. 20-2

The cycle of a steam power plant using dry saturated steam is shown on the *T-s* diagram in Fig. 20-2. The heating of the water and the vaporization in the steam generator are represented on the diagram by the process *4-1-2*. The adiabatic process *2-3* proceeds in the steam turbine and process *3-4*—in the condenser.

The thermal efficiency of the cycle and the specific steam consumption are determined by Eqs. (19-2) and (19-3)

$$\eta_t = \frac{i_1 - i_2}{i_1 - i_2'} \quad \text{and} \quad d_{theor} = \frac{1000}{i_1 - i_2}$$

When liquid metals such as sodium and potassium, which violently react with water, are used, two intermediate circuits are employed. These circuits minimize the danger of propagation of the radioactive liquid metal in the event of an emergency in the plant. Shown in Fig. 20-3 is the schematic diagram of a three-circuit atomic power plant. The following designations are used: 1—reactor; 2—first intermediate heat exchanger; 3—coolant pump; 4—steam generator or second heat exchanger; 5—pump serving this circuit; 6—turbo-generator; 7—condenser; 8—feed pump; 9—biological shielding.

Single-circuit atomic power stations with steam-turbine plants usually employ boiling water reactors. In reactors of this type steam forms in the

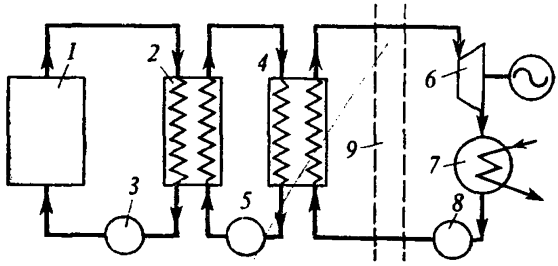


FIG. 20-3

fuel core from which it is directed to the turbine. The coolant and moderator used with boiling reactors is water.

Boiling reactors and gas-cooled reactors are used both in two-circuit and single-circuit installations. In plants of the latter type the working medium is radioactive which is most undesirable since it constitutes a danger to the attending personnel in the power station.

The heat power, or thermal capacity, of a reactor is determined by the quantity of heat transferred from the coolant to the steam generator. If the rate of coolant flow through the steam generator is equal to m kg/s, then the heat power Q_{hr} of the reactor may be found from the equation

$$Q_{hr}=m(i_{2c}-i_{1c}),$$

where i_{2c} = enthalpy of coolant at the outlet from the steam generator;
i_{1c} = enthalpy of coolant at the inlet to the steam generator.

The efficiency of atomic power plants already operating or under construction ranges from 17 to 36 per cent. The overall efficiency of an atomic power station is mainly influenced by the thermal efficiency of the vapour (steam) cycle which is not high at the present time.

In order to reduce the difference between the temperature of the feedwater circulating in the second circuit and the coolant temperature, it is advisable to practise regenerative feedwater heating with steam taken from a bleeder turbine. The fictitious regenerative cycle of such a steam-turbine plant is depicted in Fig. 20-4. The temperature of regenerative feedwater heating depends on the temperature of the coolant and it varies a lot.

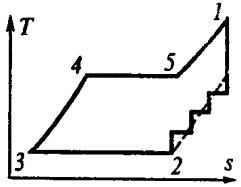


FIG. 20-4

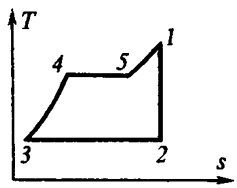


FIG. 20-5

In the first Soviet atomic power plant the maximum temperature at the centre of the fuel elements, made from metallic uranium, was taken to be 370 °C which permitted the generation of superheated steam at a pressure of 13 bar and a temperature of 270 °C.

The cycle chosen for the marine power plant installed in the *Lenin* ice breaker, rated at 44 000 horsepower, was realized at a pressure $p_1=29$ bar and a superheated steam temperature of 310 °C, which made it possible to diminish the final wetness of steam (Fig. 20-5). However the superheating of steam in the steam generator using a water coolant is practised only in special installations. Calculations indicate that atomic power stations can be operated with a higher efficiency when steam is superheated by firing fuel. For instance, in a Belgian atomic power station with a boiling reactor,

the secondary steam pressure is 47 bar, and after additional fire superheating steam temperature reaches 565 °C. The overall efficiency of the station is 37.1 per cent. The cycle realized at this atomic power station is shown in Fig. 20-6; the additional shaded area *12371* is obtained through fire superheating. But the application of fire superheating does not solve the main problem—the use of the nuclear fuel proper. In addition, the use of two sources of fuel in an atomic power station gives rise to certain problems. More promising is the superheating of steam in the reactor itself. The heat flow circuit of such an installation with a water-cooled reactor has been operating in the USSR at the Beloyarskaya atomic power station. Steam at a pressure of 90 bar is superheated in the reactor to 500 °C, making it possible to operate the station at a high efficiency (up to 35 per cent). Steam superheating in reactor is provided in other atomic power stations in many countries.

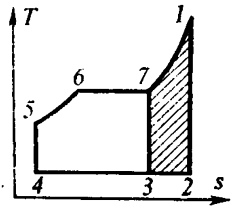


FIG. 20-6

The performance of atomic power stations differs essentially from the performance of thermal electric power stations, since the power of the reactor can be varied within a wide range and it is restricted only by conditions under which heat is removed from the fuel elements. The close relation between the performance of the reactor and steam-power circuit determines the choice of all performance characteristics of atomic power stations. An engineering, economic and thermodynamic analysis of cycles permits the selection of the most advantageous arrangement for an atomic power station.

In the plans for the development of the national economy of the USSR atomic power engineering occupies an important place. No branch of engineering develops at a higher rate than atomic power engineering. From 1954, when the world's first atomic power plant began operating in the USSR, to January 1, 1970, i.e. during 16 years, 80 atomic power stations were constructed in different countries with total power rating exceeding 15 million kW. By January 1, 1976 the total power of the world's atomic power stations had increased to 80 million kW. It is predicted that by January 1, 1980 the power rating of atomic power stations will reach 300 million kW.

At the present time uranium and plutonium are not used effectively enough, since atomic power stations employ thermal-neutron and slow-neutron reactors. Better results are obtained with fast-neutron reactors which have the notable capability of breeding nuclear fuel. In addition, fast-neutron reactors permit the use of uranium-238 and thorium-232 in the fuel cycle enabling a much greater exploitation of the natural reserves of nuclear fuel. The construction of atomic power stations using fast-neutron reactors is the main line to be pursued in the further development of atomic power in the USSR. This new branch of the national economy is to be given priority in the future.

20-2. Cycles of Vapour (Steam)-Gas Power Plants

Steam-gas power plants are typical binary installations with a cycle area ratio close to unity*.

Fuel combustion products are used as the working media in these power plants. The hot gases in gas turbines are directed to steam generators to produce steam.

Investigations have shown that gas-steam power plants are thermodynamically effective, compared with pure gas-turbine plants where the heat of the high-temperature flue gases is not utilized or with pure steam power plants having a relatively low initial steam temperature. So the reason for the efficiency of a steam-gas power plant is the use of the products of fuel combustion as a working medium in the high-temperature region and steam as a working medium in the low-temperature region. Such a distribution of functions between gas and steam yields positive results.

As is well known, the maximum thermal efficiency of a heat engine or the maximum output of mechanical work is obtained in a plant operating on the reversible Carnot cycle.

An ideal steam-gas cycle corresponding to the reversible Carnot cycle in which the temperatures of heat addition and rejection are constant is represented by area *1234* on the *T-s* diagram shown in Fig. 20-7. Area *12541* represents the gas part of the cycle and area *345*—the steam part of the binary cycle. During the process represented by line *4-5* heat is transferred from the gas part to the steam part. If we assume a temperature $t_2 = 10$ °C, and $t_1 = 800$ °C, the thermal efficiency of the Carnot cycle is equal to 0.74. It is however difficult in practice to realize the Carnot cycle and in real conditions it is only possible to construct installations which approach this cycle to some degree.

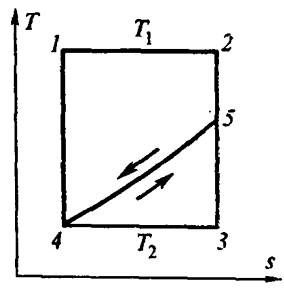


FIG. 20-7

The schematic diagram of a steam-gas power plant operated with separate combustion product and steam circuits is represented in Fig. 20-8. In a power plant of this kind air, compressed in compressor *1*, is delivered to the combustion chamber of a high pressure-fired steam generator *2* working on gas or liquid fuel at constant pressure.

A fraction of the heat from the fuel combustion products is used in the steam generator to produce and superheat steam, so that at the inlet to the gas turbine *3* the temperature of the gases drops to a preset value. Each of the working media—the steam and the fuel combustion products—flow along independent circuits and the only interaction between them is the exchange of heat in surface-type heat exchangers.

* By the term area ratio is meant the ratio of the area representing a given cycle on the *T-s* diagram to the area of the Carnot cycle realized in the same temperature interval.

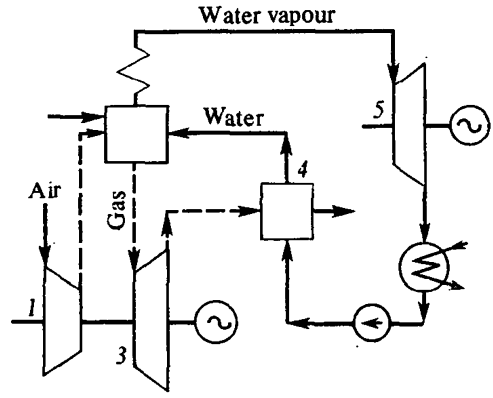


FIG. 20-8

The heat contained in the exhaust gases from the gas turbine is used to heat feedwater in the steam part of the binary-cycle power plant in gas-to-water heater *4*. Electric power is produced in two generators rotated by steam turbine *5* and gas turbine *3*, with some of the power developed by the gas turbine being expended to drive the air compressor.

The thermodynamic cycle of the gas-steam power plant consists of two cycles, the gas cycle represented by area *a-b-c-d-a* and the steam cycle depicted by area *1-2-3-4-5-6-1* (Fig. 20-9). The heat of the fuel burnt in the combustion chamber of the steam generator and added in the cycle is represented on the *T-s* diagram by area *f-g-m-g-f*. This heat is divided into the heat of fuel added in the gas part of the binary cycle, area *a-i-m-d-a*, and the heat of fuel added in the steam cycle and represented by area *f-g-i-a-f*. In the water vapour (steam) cycle the curve *4-5* represents the process of regenerative feedwater heating in the gas-to-water heater by the heat contained in the flue gases from the gas turbine, released in the process *b-c*.

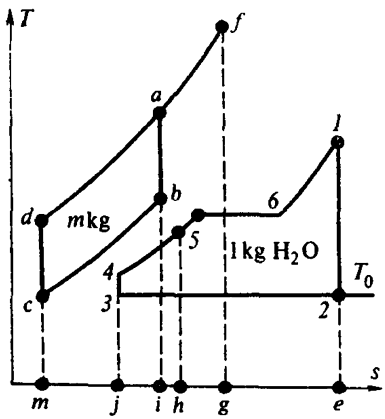


FIG. 20-9

The useful work of the vapour cycle

$$l'_w=(i_1-i_2)_{st\,t}-(i_4-i_3)/\eta_p.$$

The useful work of the gas cycle is

$$l'_g=m[(i_a-i_b)\eta_{g\,t}-(i_d-i_c)/\eta_c],$$

where $\eta_{st\,t}$, $\eta_{g\,t}$, η_p, η_c are respectively the internal relative efficiencies of the steam turbine, gas turbine, pump and compressor.

The theoretical quantity of heat added to the working media is equal to

$$q_1=m(i_a-i_d)+(i_1-i_5).$$

Knowing all these quantities, we can write the formula for the thermal efficiency of the binary water-gas cycle

$$\eta_t = \frac{(i_1 - i_2) + m(i_a - i_b) - (i_4 - i_3) - (i_d - i_c)}{(i_1 - i_5) + m(i_a - i_d)}.$$

To heat 1 kg of water, it is necessary to use a quantity of heat from m kg of gas. The ratio of m kg of gas to 1 kg of H_2O is called the *rate of gas flow* and is determined from the heat balance equation of the gas-to-water heater

$$m = \frac{i_5 - i_4}{i_b - i_c}.$$

Shown in Fig. 20-10 is the cycle of a water-gas power plant in which it is possible to use high pressure-fired steam generators by which are meant boiler units in the furnaces and flues of which a pressure of 5 bar and above is created and maintained. This intensifies the processes of fuel combustion and heat exchange and also makes it possible to decrease substantially the size of the boiler unit. Such installations ensure an electric station efficiency of up to 48-50 per cent. Area *1* represents the work input of the gas part of the binary cycle, and area *2*—of the steam part.

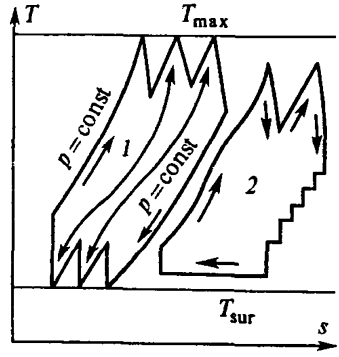


FIG. 20-10

It can be seen from Fig. 20-10 that the real cycle of a steam-gas power plant differs from the ideal cycle in the multi-stage addition of heat in the gas part, in that flue gas temperature is higher than the temperature of the feedwater, in the increase of entropy upon compression and expansion of the working medium, in that steam is superheated at the expense of additional fuel combustion, and also in the regenerative heating of feedwater.

The use of water-gas power plants improves the heat flow diagram of an electric station, raises its efficiency and reduces considerably the capital expenditures involved in construction. The most effective water-gas power plants are those incorporating high pressure-fired steam generators and in which the exhaust gas is directed from the gas turbine into the furnaces of the boiler units. The steam sections of such power plants can be operated with steam pressures of up to 240 bar and temperatures of 580 °C, with intermediate steam reheat up to 565 °C. The use of steam and gas heat regeneration considerably increases the efficiency of the installations and the efficiency of the power plant can reach 0.4-0.45 or more.

Compared with boiler units of the conventional type, a power plant with high pressure-fired steam generators has a number of advantages: the installation is of a smaller size, the consumption of metal is reduced, etc. These power plants offer a considerable saving of fuel, compared with steam-

turbine and gas-turbine power plants. Even at the present time water-gas power plants allow an efficiency of 0.33-0.36 making it possible for these installations to compete with steam-turbine plants operated at a pressure of 130 bar and a steam temperature of 565 °C. By increasing the initial gas temperature in gas turbines to within 800-900 °C, using multi-stage air compression, intermediate heat addition and regeneration of heat in the gas and steam parts and by improving the bladings of compressors and gas turbines, the efficiency of a steam-gas power plant can be raised to about 0.48.

Due to their inherent advantages, steam-gas power installations will be widely used in the near future in the power-generating industry in the USSR.

20-3. MHD-Generator Cycles

The idea of generating electric power by passing a conducting liquid, or plasma, through a magnetic field is not a new one. It is based on the well-known principle that an electromotive force is induced in a conductor when it crosses the lines of force of a magnetic field.

Plasma originates as a result of the ionization of atoms due to the detachment of one or several electrons. Plasma can be obtained in several ways: by heating a gas to high temperatures with an electric arc, by a high-voltage electric discharge, by high-frequency electromagnetic induction and also by bombarding a gas with particles at a low pressure.

Consequently, plasma is a dissociated gas whose atoms are separated into ions and electrons. The negatively charged electrons and the positively charged ions are interrelated and they behave as free charges, that plasma on the whole is neutral, but is at the same time a conductor. However in a plasma engine the gas is usually not completely ionized and contains neutral atoms. Such a gas is referred to as *low-temperature plasma.* Thus, low-temperature plasma is an electrically neutral mixture of electrons, ions and neutral atoms. Plasma is capable of interacting with electric and magnetic fields. This property of plasma is used in engines where under the influence of an electric field the ions move to the cathode, and the electrons to the anode.

A magnetohydrodynamic (MHD) generator is based on the flow of an ionized stream of gas (at a high temperature) between the poles of a high-power electromagnet. The two electrodes, arranged on both sides of the gas flow, attract the charged particles, one (the anode)—the positive, and the other (the cathode)—the negative. When the two electrodes are connected by means of a conductor an electric current is induced in the circuit.

The gas MHD generator has significant advantages, compared with a conventional steam-turbine plant. In a steam-turbine plant the chemical energy of fuel is first converted to the internal energy of the combustion products, and this is partly transferred in the boiler unit to water and the generated steam, and the energy of the steam generates electric power in

the turbo-generator. The working medium in a MHD generator is an ionized conducting gas moving in a magnetic field and serving simultaneously as a conductor, the result of which is a simple design for the power plant. In addition, the use of higher temperatures in the combustion process and the absence of moving parts in the MHD generator raise the effective efficiency.

Ionized gases are not good conductors. So, for instance, at a temperature of 2700 °C and a pressure of 3 bar the electrical conductivity of air with an addition of about 1 mole per cent* of potassium is 10^6 times smaller than the electric conductivity of copper. That is why the gaseous products of combustion must have additives with low ionization potentials, such as cesium or potassium, to ensure sufficiently high electric conductivities. The electric conductivity of a gas depends on the degree of ionization and the elastic cross-section of electron scattering.

The method of collecting current is not the same for ionized gaseous and metallic conductors. In a conventional alternating-current generator the current is collected by brushes. With a gaseous current conductor the electrodes must be at the very high temperature of 2700 °C. The problem of keeping the magnetohydrodynamic duct of the MHD generator intact at these temperatures presents one of the main difficulties in any practical application of the principles of magnetohydrodynamics. In this connection the industry has the task of finding materials with high melting point temperatures. Thus, in order to produce electric power in MHD generators there are two central problems still to be solved, associated with the electric conductivity and behaviour of materials at temperatures around 2700 °C. Not less important is the problem of creating a high-intensity electric field since the electric conductivity of plasma is relatively low and the velocity of plasma flow along the duct of the magnetohydrodynamic (MHD) generator is also relatively low.

The schematic diagram of an open-cycle MHD plant firing pulverized fuel is shown in Fig. 20-11. An idealized single-shaft turbo-generator unit is shown in the illustration. To ensure efficient use of the heat from the fuel, a steam power section is included in the plant, which makes use of the heat from the gases leaving the MHD generator. The steam section of the plant has a three-cylinder turbine.

The pulverized fuel is delivered into combustion chamber *1* of the MHD generator. Air at a pressure of up to 10 bar is fed into the combustion chamber by compressor *13*. On its way to the combustion chamber the compressed air passes through tubular regenerator *3* where it heats to 2030 °C. In the combustion chamber the temperature of the gases, products of combustion,

* The molar fraction N_i of component i is equal to the ratio of the number of moles n_i of this component to the sum of the numbers of moles $(n_1+n_2+\ldots+n_k)$ of all k components of the mixture and is determined by formula $N_i=\dfrac{n_i}{n_1+n_2+\ldots+n_k}$. The mole per cent, or the molar per cent concentration, is $100\,N_i$.

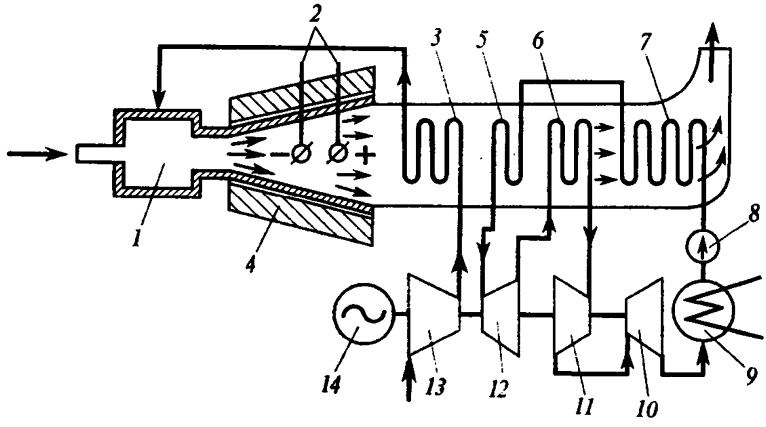


FIG. 20-11

reaches 2930 to 3030 °C. The gases at this temperature pass into the duct of the direct-current MHD generator *4* where they expand to atmospheric pressure, their temperature dropping to 2400 °C. Then the gases flow successively through heat regenerator *3*, steam superheaters *5* and *6* and steam boiler *7* in which the gases cool to 150 °C. The steam generated in the boiler passes in turn through the high-pressure cylinder *12* from which steam is directed to flow into reheater *6*, medium-pressure cylinder *11* and low-pressure cylinder *10*. From the turbine exhaust duct steam flows into condenser *9* from which water (condensate) is again delivered to the boiler by feedpump *8*. The electric current generated in the MHD generator is collected by two special busbars *2*. The electric generator *14* is driven by the three-cylinder steam turbine. The replacement of the vapour cycle of an MHD generator with a vapour-gas cycle appreciably reduces the specific consumption of heat in the generation of electric power in the generator.

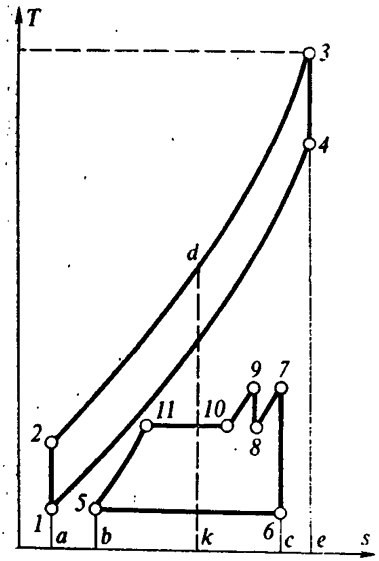


FIG. 20-12

The cycle of the MHD generator is represented on the *T-s* diagram shown in Fig. 20-12. The compressor compresses air in the process *1-2*. Then the compressed air is heated in heat regenerator to point *d* (process *2-d*). In the combustion chamber the temperature of the working medium is raised to 2930-3030 °C (point *3*). Area *d3ekd* represents the heat released upon fuel combustion. The gases formed in the combustion chamber flow

into the duct of the electric generator, passing through a strong, or high-intensity, magnetic field. Downstream from the duct of the MHD generator the temperature of the working medium drops to the value at point *4*. In an ideal MHD generator the heat converted into electric power is equivalent to area *12341*. The efficiency of such an MHD generator is determined by the ratio of the areas

$$\eta_{MHD}=\frac{\text{area } 12341}{\text{area } d3ekd}.$$

The heat from the gases leaving the MHD generator is used in the steam power plant and the ideal cycle realized in it is represented on the *T-s* diagram by area *5111098765*. The utilization of heat in the steam power plant raises the efficiency of the MHD generator to 55-60 per cent or more. If the gases leaving the MHD generator are used in a vapour-gas power plant, then the efficiency of the entire direct-energy conversion system can be further increased by several per cent.

Thus, magnetohydrodynamic systems, also referred to as direct-energy conversion systems, in which ionized plasma is used, can be operated only at high temperatures which means the use of high melting point materials. At the present time the problem of creating such high-temperature refractory materials capable of withstanding very high temperatures awaits solution.

Typical Questions to Chapter Twenty

1. What substances are used in nuclear reactors to produce nuclear power (or energy)?
2. When and where was the world's first atomic power plant constructed? Give a description of its cycle.
3. Give a description of a two-circuit atomic power plant.
4. What substances are used as coolants in nuclear reactors?
5. Why is it not yet possible to operate atomic power stations at high efficiency?
6. Where is steam superheated in an atomic power plant?
7. What cycle should be realized to operate a heat engine with a maximum efficiency?
8. Why is the efficiency of a plant increase if the vapour-gas cycle is realized?
9. Give a description of the vapour-gas cycle.
10. Give a description of a vapour-gas power plant incorporating a high pressure-fired steam generator.
11. What is meant by high-temperature and low-temperature plasma?
12. Give a description of a gaseous magnetohydrodynamic plant.
13. What methods are used to increase the ionization of a gas?

CHAPTER TWENTY ONE

REFRIGERATION CYCLES

21-1. Performance Fundamentals of Refrigerating Plants

In connection with the second law of thermodynamics it was noted (see Chapter VIII) that by realizing a reverse Carnot cycle it is possible to transfer heat from a low-temperature source, or sink, to a high-temperature source by expending mechanical work. Machines that continuously maintain the temperature of bodies below the temperature of the surrounding medium are called *refrigerating machines.*

Artificial cooling of premises and various bodies finds a wide application in the national economy (for instance, in the construction of underground railroads, in coal fields, mines, in the chemical and gas industries, in machine-building plants where parts of machines are heat-treated at low temperatures). Cold is of greati mportance in the preservation of food products. Air conditioning creates favourable conditions in industrial and public buildings, etc. Cold is produced by means of various installations in which gaseous bodies are used as working media.

Refrigerating plants can be separated into two groups. In the first group are the gas or air refrigerating plants by means of which cold was first produced in industry. Due to their insignificant refrigerating effect and their large size of individual apparatus such installations have not been widely used.

The second group includes vapour-compression refrigerating installations. The working media (refrigerants) of such machines are the vapours of various substances: ammonia (NH_3), carbon dioxide (CO_2), sulfurous anhydride (SO_2), freons (fluoro-and-chlorium derivatives of hydrocarbons), a characteristic representative of the latter group of refrigerants being freon-12 (CF_2Cl_2), etc. Vapour-compression refrigerating installations, highly reliable in operation, have been widely used in industry.

In addition to air (gas)-compression and vapour-compression machines there are refrigerating plants with other principles of operation: steam-jet and absorption refrigerating machines. In these cold is produced from the heat of some high-temperature working medium not by expending mechanical work.

In a refrigerating installation employing the steam-jet cycle the refrigerant is compressed by using the kinetic energy of a jet of working vapour of some substance. A steam-jet refrigerating installation is characterized by a low degree of thermodynamic efficiency and is rarely used in industry. Absorption refrigerating installations have been more widely used. In these energy in

the form of heat is used to produce the refrigerating effect, just as in steam-jet installations.

In distinction to a heat engine, a refrigerating plant is operated on a reverse, or refrigeration, cycle, with the most perfect cycle of this kind being the reversible reverse Carnot cycle (Fig. 21.1).

The amount of heat q_2, added to the refrigerant in the process *1-4*, is removed from the bodies being chilled; this amount of heat is represented by area *51465*. In the process represented by line *2-3* the heat removed from the refrigerant, q_1, is represented on the diagram by area *23652*. This heat is transferred to the high-temperature source at a temperature, equal to the constant temperature maintained in the process *3-2*. Area *12341* is equivalent to the amount of mechanical work expended in the cycle.

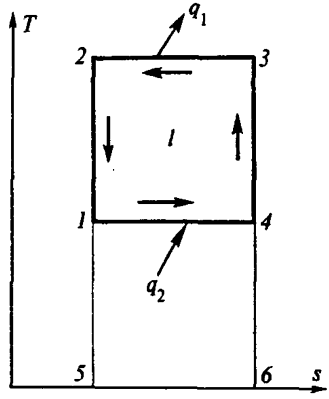


FIG. 21-1

The degree of perfection of the reverse cycle is characterized by the *refrigerating factor* or the *coefficient of performance*

$$\varepsilon=\frac{q_2}{l}.$$

The more heat is removed from the chilled bodies, q_2, and the less mechanical work is involved in the process, or the greater is the refrigerating factor ε, the more perfect is the refrigeration cycle. The refrigerating factor, or the coefficient of performance, of an arbitrary reverse cycle is smaller than the coefficient of performance of a reverse Carnot cycle.

21-2. Air (Gas)-Compression, Steam-Jet and Absorption Refrigerating Installations

Shown in Fig. 21.2 is the schematic diagram of an air-compression refrigerating installation in which the working medium is air, the most convenient, harmless and available working medium. The air-compression refrigerating installation performs in the following way. The air, cooling room *1*, is compressed in compressor *2*, with the result that its temperature rises. The compressed air is discharged at a constant pressure into heat exchanger *3* in which it is cooled by water to the temperature of the surrounding medium. Then compressed air passes into expansion cylinder, or expander, *4* in which it expands to the initial pressure. As the compressed air expands its temperature drops to minus 60 or minus 70 °C and the cold air is directed to cool the room, where, upon heating, it passes again to the compressor.

The ideal cycle of an air-compression refrigerating installation is plotted on the *p-v* and *T-s* diagrams shown in Figs. 21-3 and 21-4.

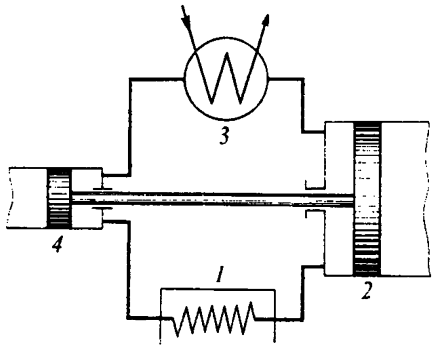


FIG. 21-2

In the process represented by line *1-2* air is compressed adiabatically from pressure p_1 to p_2. During the isobaric process *2-3* heat is rejected from the air to an external source and its temperature decreases from T_2 to T_3. Upon adiabatic expansion in the process represented by line *3-4* the air cools additionally from the temperature T_3 to T_4. Further, during the isobaric process *4-1* heat is removed from the cooled room (high-temperature source), with the result that the air heats from T_4 to T_1.

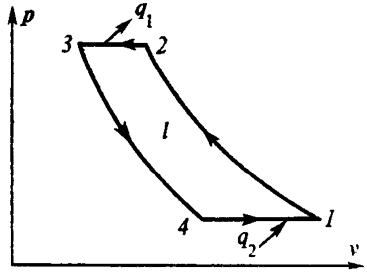


FIG. 21-3

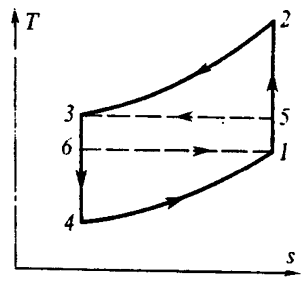


FIG. 21-4

The work expended to realize the air-compression cycle is equal to the difference between the amounts of heat q_1 and q_2. Assuming heat capacity to be constant, we obtain

$$q_1 = c_p(T_2 - T_3), \quad q_2 = c_p(T_1 - T_4),$$
$$l = q_1 - q_2 = c_p(T_2 - T_3) - c_p(T_1 - T_4).$$

Then the coefficient of performance of the cycle is equal to

$$\varepsilon = \frac{q_2}{l} = \frac{T_1 - T_4}{(T_2 - T_3) - (T_1 - T_4)} = \frac{1}{[(T_2 - T_3)/(T_1 - T_4)] - 1}.$$

From the adiabatic processes *1-2* and *3-4*

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(k-1)/k} \quad \text{and} \quad \frac{T_3}{T_4} = \left(\frac{p_3}{p_4}\right)^{(k-1)/k}$$

but $p_2=p_3$ and $p_1=p_4$, then

$$\frac{T_2}{T_1}=\frac{T_3}{T_4}$$

or by the properties of a proportion

$$\frac{T_2-T_3}{T_1-T_4}=\frac{T_2}{T_1}=\frac{T_3}{T_4}.$$

Finally we have

$$\varepsilon=\frac{1}{(T_2/T_1)-1}=\frac{T_1}{T_2-T_1}, \tag{21-1}$$

where T_1 = temperature in the room being cooled or temperature of air drawn into the compressor;
T_2 = temperature of compressed air.

The cycle of an air-compression refrigerating installation is externally reversible since heat is rejected into the surrounding medium at a constant temperature, equal to T_3 in the limit. Heat is added to the working medium from the cooled room in which a constant temperature must be maintained, not higher than T_1. Thus, due to the imperfection of the cycle after the compressor the air must be overheated by the temperature difference T_2-T_3 and cooled below the temperature of the cooled room by the temperature difference T_1-T_4. The most effective process of heat rejection would be the isothermal process *5-3* (Fig. 21-4) and the process of heat addition—would be the isothermal process *6-1*. Also it would be possible to realize the indicated processes reversibly in the limit. But the cycle *1-5-3-6-1* is the reversible Carnot cycle. So, it is again seen that the reversible Carnot cycle is the most perfect cycle for a refrigerating plant.

Compared with the Carnot cycle, the ideal cycle of a refrigerating plant involves an additional expenditure of work, equal to the sum of areas *2352* and *1641*. The quantity of heat removed from the cooled room per cycle will be smaller than the amount of heat removed in the Carnot cycle by the magnitude of area *1641*.

The coefficient of performance of the reverse Carnot cycle, as it follows from Eq. (21-4), is equal to

$$\varepsilon^{\text{Carnot}}=\frac{q_2}{l}=\frac{q_2}{q_1-q_2}=\frac{T_1}{T_3-T_1},$$

and since $T_3<T_2$ it follows that

$$\varepsilon^{\text{Carnot}}>\varepsilon.$$

The cycle of an air-compression refrigerating installation is imperfect from the thermodynamic viewpoint, the efficiency of the installation is low and it is of cumbersome design.

Shown in Fig. 21-5 is the schematic diagram of a steam-jet refrigerating installation. The vapour of the working medium flows from evaporator *1*

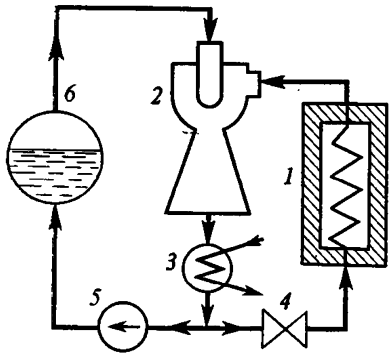


FIG. 21-5

to the mixing chamber of ejector *2* into which steam is delivered through a nozzle from boiler *6*. The mixture of vapours forming in the combining chamber is compressed in the diffuser of the ejector and passes into condenser *3* where the mixture condenses giving away its heat of vaporization. At the condenser outlet the liquid separates into two flows. One of the liquid flows is throttled in expansion valve *4* in which the pressure and temperature drop and a small fraction of the liquid turns into steam. The forming wet steam with a small dryness fraction (up to 10 per cent) flows into evaporator *1* and serves as the refrigerant. The other condensate flow is directed by feed pump *5* into boiler *6* where it is converted into steam at the expense of heat added from the outside and the steam formed passes again to the injector nozzle.

In evaporator *1* the refrigerant, a wet steam, taking up heat from the cooled bodies, evaporates at a constant pressure and then is delivered as dry steam to the mixing chamber of the ejector, and the cycle is repeated. In a steam-jet refrigerating installation energy is expended not in the form of mechanical, or shaft, work, but in the form of heat. The coefficient of performance of a steam-jet refrigerating installation is determined by the equation

$$\varepsilon = \frac{q_2}{q_1}, \tag{21-2}$$

where q_2 = quantity of heat added to 1 kg of the refrigerant in the evaporator;

q_1 = quantity of heat added to the steam in the boiler per 1 kg of the refrigerant.

The important advantage of steam-jet refrigerating installations is the absence of a costly compressor. In addition, these installations are distinguished by simple design, reliable performance, and by the small size of all component units, but their thermodynamic perfection and thermal efficiency are not high. By using an appropriate working medium as refrigerant in a steam-jet refrigerating installation very low temperatures are obtainable.

The next type of refrigerating machines is the installation operated on the absorption refrigeration cycle. By *absorption* is meant the process where the entire mass of one substance is absorbed by another substance. Absorption refrigerating installations differ substantially from all other types of refrigerating machines in that their design is simple. In absorption refrigerating installations the refrigerating effect is obtained not at the expense of

energy in the form of mechanical work, but energy is in the form of heat. For absorption refrigeration units solutions of two substances are chosen which have different boiling points and which may be completely dissolved in each other. The low-boiling point liquid is used as the refrigerant, and the other liquid, possessing a higher boiling point, as an absorbent.

The boiling point of the binary solution depends at a given pressure on the concentration of the solution. The properties of binary systems are represented on the so-called diagrams of state on which the concentration of the refrigerant C is plotted along the x-axis, and the pressure p or temperature t (Fig. 21-6)—along the y-axis. The origin of coordinates corresponds to the boiling point of the pure absorbing substance, absorbent, point A ($C_1=1, C_2=0$), and point B represents the temperature of the pure substance of the refrigerant ($C_2=1$, $C_1=0$; $C_1+C_2=1$). The curve AaB represents the state of the liquid phase or the line of the boiling solution at the given

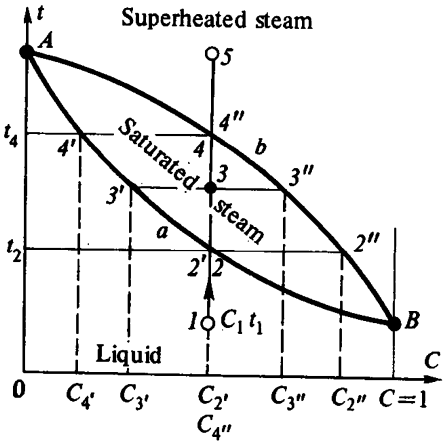


FIG. 21-6

pressure, and line AbB corresponds to the line of condensation (of dry saturated vapour) or the line of the vapour phase when the two phases are in equilibrium.

Let us consider the process of vaporization of the binary mixture on the t-C diagram. We shall assume that the initial state of the mixture investigated is characterized by point *1* with a concentration C_1 and temperature t_1. If heat is added to this solution, its temperature shall rise along line *1-2*. At point *2*, located on the boiling liquid curve, the solution shall begin to boil and at point *2''* the temperature of dry saturated vapour shall be equal to temperature of the liquid. The composition of the vapour at point *2''* differs considerably from the composition of the boiling liquid at point *2*. Consequently, point *2* represents the state of the boiling liquid with composition $C_{2'}$, and the equilibrium state of dry saturated vapour with composition $C_{2''}$, where $C_{2''}>C_{2'}$.

As heat addition is continued the content of the second component in the boiling liquid diminishes, and the process of vaporization proceeds along line *2-3*. At point *3* the binary solution represents a system consisting of the boiling liquid (point *3'*) with composition $C_{3'}$ and dry saturated vapour (point *3''*) with composition $C_{3''}$, where $C_{3''}>C_{3'}$; $C_{3'}$ and $C_{3''}$ represent equilibrium compositions respectively of liquid and vapour for the pressure p and boiling point $t_{3'}=t_{3''}$. If heat addition is continued further, point *4* may be reached where the solution is fully converted into dry saturated vapour, the composition of this vapour being the same as the initial composition of the binary liquid mixture ($C_{4''}=C$). The composition of the boiling liquid which is in equilibrium with the dry saturated vapour with composition $C_{4''}$ is $C_{4'}$. With further heat addition superheating of the vapour takes place (point *5*).

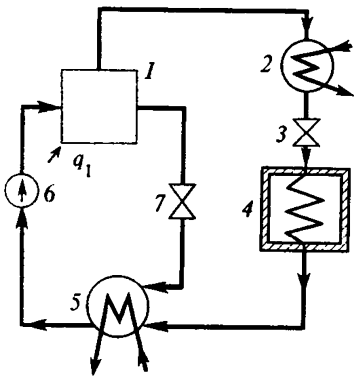


FIG. 21-7

Thus, saturated vapour forms in the evaporator, located in the chilled room, with a high concentration $C_{2''}$, the state of which is represented by point *2''*, then this vapour can be in equilibrium with boiling liquid with a concentration $C_{2'}$. With respect to liquid having a smaller concentration $C_{4'}<C_{2'}$, boiling at temperature t_4, this vapour is subcooled; therefore when the two phases come into contact vapour condensation takes place, resulting in full absorption of the vapour by the liquid. During this process the heat of condensation is rejected at the temperature of the liquid, t_4, which is higher than the vapour temperature t_2. As a consequence heat is transferred from a body at a lower temperature (high-concentration vapour) to a body at a higher temperature (low-concentration liquid).

In connection with the above, the schematic diagram of an absorption refrigerating installation is illustrated in Fig. 21-7. An absorption refrigerating installation performs in the following way. When heat q_1 is added in vapour generator *1* the refrigerant evaporates from the binary mixture in the form of almost dry saturated vapour and passes to condenser *2* where the vapour condenses completely, transferring the heat of vaporization to the cooling water. The liquid refrigerant is throttled in expansion valve *3* with a resulting drop in its pressure and the temperature of the liquid drops to a temperature lower than that maintained in the chilled volume *4*. Upon addition of heat q_2 from the chilled bodies, the refrigerant evaporates, turning into wet vapour, and passes to absorber *5*, where it gives away its heat of absorption to the cooling water and is completely absorbed by the absorbent. As the refrigerant is being absorbed by the absorbent, the solution with a great concentration is delivered by pump *6* into vapour generator where, at the expense of the heat q_1 added from an external source, the

refrigerant is evaporated from the solution and is directed to condenser *2*. The absorbent with a weak concentration of refrigerant is directed through the expansion valve *7* to absorber *5* where the pressure and temperature of the mixture decrease. In the absorber the concentration of the refrigerant rises and it is again delivered by pump *6* into the vapour generator.

The coefficient of performance or the heat utilization factor of an absorption refrigerating installation is determined from equation

$$\varepsilon = \frac{q_2}{q_1}, \tag{21-3}$$

where q_2 = quantity of heat added to the refrigerant from the bodies being chilled in the installation;

q_1 = quantity of heat spent in the vapour generator.

The coefficient of performance is equal to the ratio of the heat removed from the chilled bodies to the heat spent in the vapour generator.

Absorption refrigerating installations are less perfect thermodynamically than vapour-compression machines, but they are of single design, are reliable in service and are cheaper to manufacture and so are widely used, for instance, for domestic refrigerators.

21-3. Vapour-Compression Refrigeration Cycle

The most widespread refrigeration units for cooling bodies to a temperature of -20 °C are installations which use as refrigerants low-boiling liquids, for instance, ammonia, freons, sulfurous anhydride and others, at low pressures (preferably close to atmospheric).

The schematic diagram of a vapour-compression refrigerating installation operated with ammonia vapour (NH_3) is shown in Fig. 21-8. The notations used on the diagram are as follows: *1*—compressor; *2*—condenser; *3*—expansion valve; *4*—chilled volume (evaporator).

The compressor is used to compress dry saturated vapour or wet vapour with a large dryness fraction along adiabat *1-2* to the state of superheated vapour at point *2* (Fig. 21-9). The compressor discharges the vapour into the condenser where it condenses completely (turns into liquid) (process *2-3-4*). From the condenser, liquid ammonia passes through the expansion valve where it is throttled, resulting in a drop of temperature and pressure. Then the liquid ammonia at a low temperature passes into the cooler where heat is transferred to it (in the process *5-1*), the ammonia evaporates and cools the brine which circulates in the chilled compartments. The throttling process, being an irreversible one, is represented on the *T-s* diagram by the broken curve *4-5*.

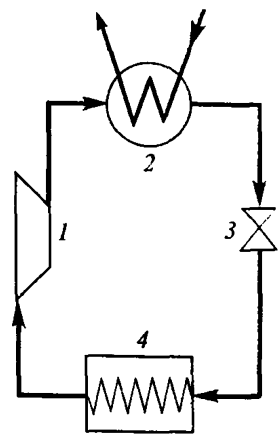


FIG. 21-8

A vapour-compression refrigerating installation does not incorporate an expander and the working medium is throttled in the expansion valve. The replacement of the expander with an expansion valve is accompanied by an increase of entropy, which causes a certain loss of refrigerating capacity, but this replacement greatly simplifies the installation. It enables easy control of vapour pressure and makes it possible to maintain an irreversible temperature in the cooler, since in the two-phase region the refrigerating effect of throttling will be the same as that of adiabatic expansion. If an expander were present, the process would proceed along adiabat *4-9*.

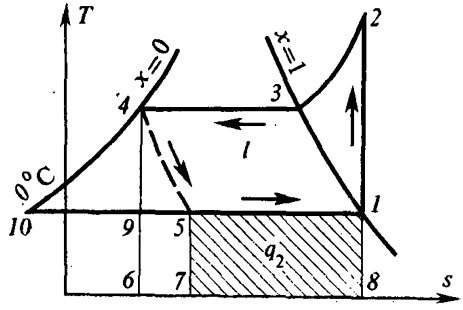


FIG. 21-9

The loss of refrigerating capacity due to the replacement of the expander with an expansion valve is measured by area *95769*, which is why the amount of heat q_2 transferred to 1 kg of ammonia from the chilled bodies diminishes and is represented by area *75187* $(i_1-i_5)=(i_1-i_4)$. The amount of heat q_1 removed by the cooling water in the condenser is represented on the diagram by area *64286*. The work expended to realize the refrigeration cycle, $l'=q_1-q_2=$ area *6412576* = area *1041210* $=i_2-i_1$. The equality of areas *6412576* and *1041210* stems from the condition that throttling of ammonia results in that the enthalpy at point *5* shall be equal to the enthalpy at point *4*.

The coefficient of performance, or the refrigerating effect, of an ammonia compression refrigerating machine

$$\varepsilon=\frac{q_2}{l'}=\frac{\text{area } 75187}{\text{area } 1041210},$$

where $q_2 = i_1-i_5=i_1-i_4=$ amount of heat transferred to the ammonia vapour in the cooler;

$l' = i_2-i_1=$ work expended upon adiabatic compression of ammonia vapour in the compressor.

It follows from this that the coefficient of performance of the refrigerating plant is equal to

$$\varepsilon=\frac{i_1-i_4}{i_2-i_1}. \qquad (21\text{-}4)$$

The values of the enthalpies in Eq. (21-4) are determined on the *i-s* diagram or from tables compiled for ammonia vapour. Vapour compression refrigerating installations have a great advantage over refrigerating installations operated on the air-compression cycle. They are of compact design, are cheap and operate with a higher coefficient of performance.

21-4. Cryogenic Engineering

Liquefaction of gases is of great importance for the national economy. In order to liquefy any gas, its temperature must be lowered below the parameters at the critical point. Only then is simultaneous equilibrium coexistence of liquid and vapour phases possible. Gases can be liquiefied with the aid of a machine operating on a reverse of refrigeration cycle. A theoretically minimum amount of mechanical work will be expended in the reverse cycle.

Let us assume that a gas is cooled from temperature T_1 (point *3*, Fig. 21-10) to temperature T_2 (point *1*). From the state at point *3* the gas is compressed isothermally (point *4*), with the heat $q_1=T_1(s_3-s_4)$ being transferred to the surrounding medium. The following adiabatic expansion (point *1*, process *4-1*) results in the production of liquefied gas. Such an arrangement involves the expenditure of minimum work l_{min}. The minimum

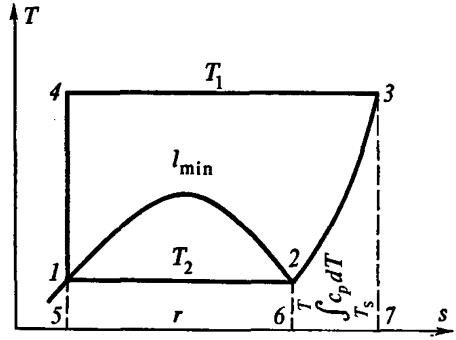


FIG. 21-10

amount of work involved in gas liquefaction is equal to the sum of the amounts of work spent to cool the gas and remove from it the entire heat of vaporization:

$$l_{min}=l_{3\text{-}2}+l_{2\text{-}1}.$$

The minimum work input in an ideal cycle, represented in Fig. 21-10 by area *32143*, is equal to the difference between two areas: area *37543*,

equal to the product $T_1(s_7-s_5)$, and area *321573*, equal to $q_2=\int_{T_1}^{T_2} c_p\,dT+$ $+r=i_3-i_1$, whence

$$l_{min}=T_1(s_7-s_5)-(i_3-i_1).$$

The work needed to liquefy a gas in a real cycle is greater than the amount of work required in the ideal cycle, and the difference between the amounts of work is determined by the loss of availability due to the irreversibility of the process:

$$l_{ir}=l_{rev}+T_0\Delta s,$$

where T_0 = temperature of the surrounding medium.

The ideal cycle cannot be realized in practice, since to ensure the state of substance at point *4* pressures of tens and hundreds of bars must be created so as to get on the liquid boundary line in the adiabatic process *4-1*. That is why it is impossible to realize this ideal cycle.

At present a great variety of different types of apparatus are available for the liquefaction of gases. Their principle of operation is based on two methods based on: the throttling effect (the Joule-Thomson effect) and the adiabatic expansion of gas with work done on the surrounding medium.

The high-pressure multiple throttling cycle was first put into practice by K. Linde and is referred to as the Linde gas liquefaction method or the Linde process. The Linde system is based on the regenerative principle in which the decrease of temperature is continuously lowered upon throttling for subsequent cooling of a new portion of gas. The process of continuously lowering the temperature continues until the gas liquefaction temperature is reached.

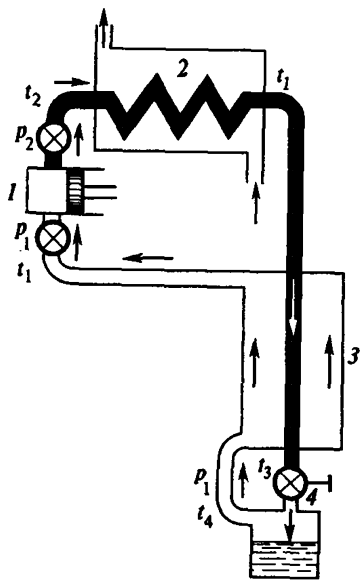


FIG. 21-11

Shown in Fig. 21-11 is the schematic layout of the simplest high-pressure multiple throttling liquefying plant based on the Linde process. In compressor *1* air is compressed adiabatically from pressure p_1 to p_2, with the temperature of the compressed air rising from t_1 to t_2. The compressed air is water-cooled in cooler *2* to the temperature t_1. The cooled compressed air passes at the pressure p_2 into the counterflow heat exchanger *3* where it is cooled to temperature t_3 by cold air.

After the counterflow heat exchanger the cooled compressed air is throttled in expansion (throttling) valve *4* to pressure p_1, with air temperature dropping to t_4. The gas

at temperature t_4 flows through the heat exchanger and heats to temperature t_1, removing heat from the high-pressure air whose temperature drops to t_3. After the heat exchanger the air at a temperature t_1 flows again to the compressor and the cycle repeats continuously. From the heat exchanger the compressed gas is directed to the expansion (throttling) valve in which continuous throttling of air takes place. Finally, the high-pressure air is cooled to such a low temperature that upon successive throttling it turns into wet vapour from which a small fraction of liquid air can be separated. This terminates the preliminary starting period and a steady-state process of air liquefaction commences.

The process of gradual air cooling is represented on the *T-s* diagram, shown in Fig. 21-12.

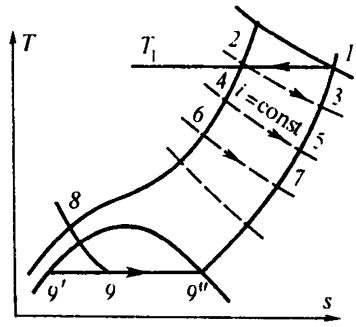


FIG. 21-12

The gas, compressed isothermally from the state at point *1* to the state at point *2*, is throttled in the expansion valve, so that the temperature of the gas drops to the temperature at the state at point *3*. The temperature of state at point *3* is several degrees below the temperature of the surrounding medium *T*. The entire throttled gas (state at point *3*) is directed to flow into a counterflow regenerator in which it cools a new portion of the gas compressed from pressure p_1 to pressure p_2 (state at point *4*). If the cooled gas in this state is then again throttled, the resulting gas (point *5*) will have a lower temperature. The gas in the state at point *5* is now used in turn to cool the liquefied gas to the state at point *6* and as a result of throttling the state at point *7* is reached, etc. In the course of some time the gas shall be in the state characterized by point *8*, and upon throttling, in the state at point *9*. Since point *9* lies in the wet vapour region, the gas consists of a mixture of boiling liquid and dry vapour. Opening the discharge valve, some quantity of liquefied gas can be obtained.

In a steady-state gas liquefaction process with single stage throttling the *liquefied-gas production factor* can be found from the equation

$$g=\frac{i_1-i_2}{i_1-i_0}, \qquad (21\text{-}5)$$

where i_1 = enthalpy of gas at a pressure of 1 bar;
i_2 = enthalpy of gas at a pressure of p_2 bar;
i_0 = enthalpy of liquefied gas at a pressure of 1 bar.

The second method, or process, of gas liquefaction consists in adiabatic expansion of the gas with transfer of work to the surrounding medium. The most perfect plant for gas liquefaction has been created in the USSR by academician P. Kapitsa. This plant is operated on the low-pressure cycle with the use of a turbine expander.*

* Zhurnal tekhnicheskoi fiziki AS of the USSR, 1939, v. 9, iss. 2.

21-5. Heat Pump

The reverse cycle can be realized not only in refrigerating machines, intended to maintain the temperature in a chilled volume at a preset value, but also in so-called heat pumps that are used to transfer the heat at a low potential, removed from the surrounding medium at the expense of external work to an external consumer at a higher temperature.

The degree of perfection of the performance of a heat pump is characterized by the ratio of the amount of heat transferred to an external consumer to the work expended to ensure such heat transfer, i.e.

$$\xi = \frac{q_1}{l} = \frac{(q_2 + l)}{l} \tag{21-6}$$

The coefficient ξ is usually referred to as the *heating coefficient*, or *heat utilization factor*, or the *coefficient of performance of a heat pump*. The performance of a heat pump does not differ in principle from that of a refrigerating installation. A heat pump is used for heating purposes in applications where a low-temperature heat source is available (for instance, water in different reservoirs; the cooling water from hydraulic generators, etc.), and it is also made use of as a source of cheap work. Utilization of the heat of low-temperature heat sources can be of some importance for the national economy in regions where great amounts of cheap electric power are generated in hydroelectric power plants. It is not worthwhile to use heat pumps for heating purposes and community heat supply when the mechanical work must be done by power taken from conventional electric stations fitted with condensing turbines.

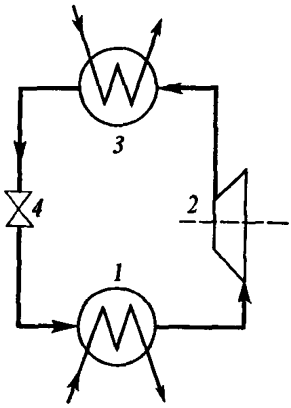


FIG. 21-13

A heat pump works as follows. The working medium which has a low boiling point (ammonia, freons) evaporates in evaporator *1* (Fig. 21-13) at the expense of heat from a low-temperature heat source. The forming vapour is directed into compressor *2* in which the temperature of the working medium rises from t_2 to t_1. The vapour at the temperature t_1 passes into condenser *3* where it condenses and transfers heat to the liquid circulating in the heating system. The forming working-medium condensate is directed to throttling valve *4* where it is throttled from pressure p_1 to p_2. From the throttling valve the liquid working medium flows again to evaporator *1*.

The ideal cycle of a heat pump is similar to the ideal cycle of the vapour-compression refrigerating plant shown in Fig. 21-9.

It is clear from Fig. 21-9 that the work spent, represented by area *1041210*, is transferred together with the heat of the low-temperature source to a body

at a higher temperature. Denoting the heat transferred to freon in the evaporator by q_2, the heat transferred to the heating system by q_1 and the work expended in the compressor by l, then

$q_1=q_2+l.$

It follows from considering the cycle that

$q_1=i_2-i_4=i_2-i_5$, and $q_2=i_1-i_5$.

The enthalpy of the working medium does not change upon throttling, therefore $i_4=i_5$, and

$l=q_1-q_2=(i_2-i_5)-(i_1-i_5)=i_2-i_1$,

whence

$$\xi=\frac{q_1}{l}=\frac{i_2-i_5}{i_2-i_1}. \tag{21-7}$$

If the heat pump is operated on the reverse Carnot cycle, the coefficient of performance is equal to

$$\xi=\frac{q}{l}=\frac{T_1}{T_1-T_2}$$

For instance, when a building is heated in winter, river water temperature $T_2\approx 280$ K and the temperature of the working medium circulating in the heating system, $T_1=350$ K, then in these conditions

$$\xi=\frac{350}{350-280}=5.0$$

A coefficient of performance of 5.0 indicates that the heat pump transfers an amount of heat equal to five times the amount of expended work to the heating system. If mechanical work is done with 1 MJ of electric power, then 5 MJ of heat is transferred to the heating system, i.e., five times more than with purely electric heating. Consequently, from the power consumption viewpoint the use of heat pumps is undoubtedly very promising and they must find wide application where it is necessary.

In a number of cases favourable conditions occur for the operation of a heat pump if a compressor is driven directly from a reciprocating internal combustion engine. In installations of this kind the water cooling the engine cylinders is used as the low-temperature heat source, and the heat of the exhaust gases is used in the waste-heat boilers of district-heating systems.

Typical Questions and Examples to Chapter Twenty One

1. Into what groups are refrigerating installations classified?
2. What is the difference between steam-jet and absorption refrigerating installations and vapour-compression machines?
3. What is meant by the refrigerating effect or the coefficient of performance?
4. Give a description of an air-compression refrigerating installation. What are its shortcomings?

5. Describe a steam-jet refrigerating installation.
6. Describe an absorption refrigerating installation. What are its advantages?
7. Describe a vapour-compression refrigerating installation.
8. Represent the ideal cycle of a vapour-compression refrigerating installation on a *T-s* diagram.
9. Describe the ideal cryogenic (deep cooling) cycle.
10. What are the peculiarities of the cascade method of gas liquefaction?
11. What are the distinguishing features of the refrigerating installation developed by academician P. Kapitsa?
12. In what cases is it expedient to use a heat pump for heating buildings?
13. Describe the ideal cycle of a heat pump.
14. What is meant by the heating coefficient? Give its definition.
15. What are the advantages of a heat pump compared with direct utilization of electric power for heating purpose?
16. What are the peculiarities and advantages of a heat pump when an internal combustion engine is used to drive the compressor?

Example 21-1. Determine the theoretical power of the engine of an ammonia compression refrigerating machine, the hourly consumption of ammonia, brine and cooling water, the coefficient of performance of the installation and the refrigerating factor of the Carnot cycle, if the refrigerating capacity of the installation is $Q=300\,000$ kJ/h. The data for solving the problem are taken from the course on refrigerating installations. The compressor of the installation draws ammonia vapour at a temperature $t_0=-10$ °C and with a dryness fraction $x_1=0.95$ and compresses the vapour adiabatically to the state of superheated vapour at the pressure $p_2=8.57$ bar. The compressor discharges the ammonia vapour into the condenser in which the cooling-water inlet temperature $t_{in}=10$ °C and outlet temperature is 20 °C. In the reducing valve liquid ammonia is throttled to $p_1=2.9$ bar, then it is directed to the evaporator, from which it flows with a dryness fraction $x_1=0.95$ to the compressor. Ammonia evaporates in the refrigerator at the expense of the heat of the brine circulating in the refrigerating chambers. At the inlet to the evaporator brine temperature $t_b=-8$ °C and at the outlet, −2 °C. The heat capacity of brine $c_b=5.0$ kJ/kg·deg (Fig. 21-9).

At the inlet to the compressor (or at the outlet from the refrigerator) ammonia vapour conditions are as follows: $p_1=2.9$ bar; $t_1=-10$ °C; $i_1=373$ kJ/kg; $r_1=1297$ kJ/kg; the conditions of the superheated ammonia vapour discharged from the compressor are: $p_2=8.57$ bar; $i_2=1805$ kJ/kg. The enthalpy of the ammonia vapour drawn by the compressor from the refrigerator

$$i_1=i_1'+r_1x_1=373+1297\times0.95=1605 \text{ kJ/kg}.$$

The work expended in the compressor to compress 1 kg of ammonia amounts to

$$l=i_2-i_1=1805-1605=200 \text{ kJ/kg}.$$

The heat rejected from the ammonia vapour in the condenser:
the heat of superheat $i_2-i_3=1805-1700=105$ kJ/kg;
the heat of vaporization $r_{3\text{-}4}=1187$ kJ/kg.
The total quantity of heat rejected in the condenser is
equal to $105+1187=1292$ kJ/kg.
At a pressure $p_2=8.57$ bar the enthalpy of liquid ammonia
$i_4=512.6$ kJ/kg (Taken from NH_3 tables).

Upon throttling in the reducing valve from 8.57 to 2.9 bar the enthalpy does not change, consequently,

$i_5=512.5$ kJ/kg.

At $p_5=2.9$ bar: $i'_5=373$ kJ/kg

$$i_5=i'_5+x_2r_{1\text{-}5}; \quad x_2=\frac{i_5-i'_5}{r_{1\text{-}5}},$$

whence

$$x_2=\frac{5125-373}{1297}=0.1075.$$

The refrigerating capacity of 1 kg of ammonia or the amount of heat spent to evaporate 1 kg of ammonia

$q_2=i_1-i_5=1605-512=1093$ kJ/kg.

The coefficient of performance of the installation is equal to

$$\varepsilon=\frac{q_2}{l}=\frac{1093}{200}=5.47.$$

With the conditions of the example the coefficient of performance of the Carnot cycle amounts to

$$\varepsilon_{\text{Carnot}}=\frac{T_0}{T_1-T_2}=\frac{263}{293-263}=8.79.$$

The quantity of ammonia circulating in the installation

$$m_s=\frac{Q}{q_2}=\frac{300\,000}{1093\times3600}=0.0762 \text{ kg/s}.$$

The theoretical power of the drive motor is

$N_{theor}=m_sl=0.0762\times135=10.28$ kW.

The amount of brine circulating in the refrigerating chambers,

$$m_b=\frac{300\,000}{3600\times5}[-2-(-8)]=2.8 \text{ kg/s}.$$

The rate of cooling water flow

$$m_w=\frac{0.0762\times1292}{4.19(20-10)}=2.35 \text{ kg/s}.$$

where 4.19 is heat capacity of water.

PART TWO

HEAT TRANSFER

INTRODUCTION

The science of heat transfer is devoted to the study of processes of heat propagation in solid, liquid and gaseous bodies. Such processes, because of their highly diversified physico-mechanical nature, are very complex and usually proceed as a whole complex of heterogeneous phenomena.

Heat may be transferred in three ways: by conduction, convection and thermal radiation. These modes of heat transfer differ profoundly in nature and are governed by different laws.

Heat transfer by conduction takes place between bodies or particles of bodies that are in direct contact and at different temperatures. The science of heat conduction by homogeneous and isotropic bodies rests on a strong theoretical foundation of simple quantitative laws, developed by well elaborated mathematics. According to the viewpoint of present-day physics, *heat conduction*, or simply *conduction*, is a molecular process. In metals, when this mode of heat transfer takes place, a leading role is played by free electrons.

It is common knowledge that when a body is heated the kinetic energy of its molecules increases. The particles in a heated part of a body collide randomly with their neighbouring particles, and transfer to them a fraction of their kinetic energy. This process gradually spreads through the entire body. For instance, if one end of a metal rod is heated, then after a time the temperature of the opposite end of the rod will also rise. The transport of heat by conduction depends on the physical properties of the body, its geometrical shape, and also on the difference between the temperatures of different parts of the body. In determining heat transfer by conduction in

real bodies, certain problems are encountered, which have not yet been solved satisfactorily in practice. They occur when heat-transfer processes take place in a heterogeneous medium whose properties vary over the volume and are temperature dependent. In addition, these difficulties increase with the complexity of the configuration of the system.

The second mode of heat transfer occurs only in fluids, i.e. gases and liquids, and is called *convection*. This mode of heat transfer takes place when the entire mass of a non-uniformly heated liquid or gas is displaced and mixed. Heat transfer by convection takes place at a greater rate when the velocity of motion of the liquid or gas is higher, as in this case a greater number of fluid particles are displaced per unit time. In liquids and gases heat transfer by convection is always accompanied by conduction, since in the course of convection particles at a different temperature are always in direct contact.

The combined mode of heat transfer by convection and conduction is referred to as *convective heat transfer*. Free (or natural) and forced convection are distinguished. If the working medium is put into motion artificially (by means of a fan, compressor, mixer, etc.), then such convection is referred to as *forced*. But if the working medium begins to move due to the difference between the densities of individual parts of the fluid upon heating, then the mode of heat transfer is referred to as *free*, or *natural*, convection.

The third mode of heat transfer is known as thermal radiation. This process of heat transfer, between two bodies separated by a medium which transmits radiation fully or partly, takes place in three stages: conversion of a fraction of the internal energy of one of the bodies into the energy of electromagnetic waves, propagation of the electromagnetic waves in space, and absorption of radiant energy by the other body. At comparatively low temperatures radiant energy is mainly transported by infrared rays.

The combination of the three modes of heat transfer is referred to as the *combined mode of heat transfer*. However the study of the laws of combined heat transfer involves rather great difficulties. Hence each mode of heat transfer is studied separately, after which it is possible to carry out calculations for combined modes of heat transfer.

CHAPTER TWENTY TWO

BASIC CONCEPTS OF CONDUCTION

22-1. Temperature Field

The phenomenon of heat conduction is a process of propagation of energy between the particles of a body which are in direct contact and have different temperatures.

Let us consider the heating of some homogeneous and isotropic body (only such bodies shall be considered below). Bodies which have uniform physical properties in all directions are said to be *isotropic*. When an isotropic body is heated, the temperatures at various points change with time and heat propagates from places at a higher temperature to places at a lower temperature. From this it follows that in general, in a solid body, the process of heat transfer by conduction is accompanied by variation of the temperature t both in space and time

$$t=f(x, y, z, \tau), \tag{22-1}$$

where x, y, z = point coordinates;
τ = time.

This function determines the temperature field in the body considered. In mathematical physics the *temperature field* means the totality of temperature values at a given point of time for all points of the space considered in which heat transfer process takes place.

If the temperature of a body is a function of space coordinates and time, the temperature field is of the *transient kind*, i.e. it depends on time

$$t=f(x, y, z, \tau); \quad \partial t/\partial \tau \neq 0. \tag{22-2}$$

Such a field corresponds to transient conduction.

If the temperature of a body is a function of the spatial coordinates only and does not vary with time, the temperature field is referred to as a *steady-state* one

$$t=f(x, y, z); \quad \partial t/\partial \tau = 0. \tag{22-3}$$

The equation of a two-dimensional temperature field of a steady-state, or stationary, field is

$$t=f(x, y); \quad \partial t/\partial z = \partial t/\partial \tau = 0;$$

and of a transient field

$$t=f(x, y, \tau); \quad \partial t/\partial z = 0; \quad \partial t/\partial \tau \neq 0.$$

In practice, problems occur when the temperature of a body is the function of just one coordinate. The equation of a one-dimensional temperature field is as follows:

of a steady-state field

$$t=f(x); \quad \partial t/\partial \tau=0 \quad \text{and} \quad \partial t/\partial y=\partial t/\partial z=0;$$

of a transient field

$$t=f(x); \quad \partial t/\partial \tau \neq 0 \quad \text{and} \quad \partial t/\partial y=\partial t/\partial z=0. \tag{22-4}$$

An example of a one-dimensional problem is heat transfer in a wall whose length and width may be considered to be infinite compared with the thickness.

22-2. Temperature Gradient

If we join together all points of a body which have the same temperature, we obtain an equal temperature surface, known as an *isothermic surface*. Isothermic surfaces never intersect. They are either closed or end at the boundary of the body.

Let us consider two isothermic surfaces closed together, with temperatures t and $t+\Delta t$ (Fig. 22-1). Moving from any point A, it can be found that the rate of temperature variation in various directions is not the same. No temperature variation is observed on an isothermic surface. But if we move along any direction S, variation of temperature is observed. The greatest temperature difference per unit length is observed in the direction normal to the isothermic surface. The limit of the ratio of temperature variation Δt to the distance between isothermic surfaces along the normal, Δn, when Δn tends to zero, is referred to as the *temperature gradient*, measured in units [deg/m]

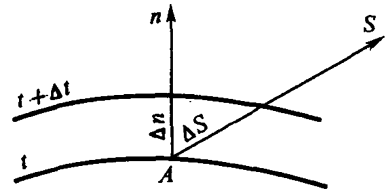


FIG. 22-1

$$\text{grad } t=\lim \frac{\Delta t}{\Delta n}\bigg|_{\Delta n \to 0}=\frac{\partial t}{\partial n}. \tag{22-5}$$

The temperature gradient is a vector normal to the isothermal surface in the direction of rising temperature and it is equal numerically to the partial derivative of temperature in that direction. The temperature gradient is assumed to be positive in the direction of increasing temperature.

22-3. Basic Law of Conduction

For propagation of heat in any body or space to take place, there must be a difference between the temperatures at different points of the body. This must also be so for heat transfer by conduction when the temperature gradient at various points of the body is not zero.

The quantity of heat dQ in J passing through an elementary area dF on the isothermal surface per time interval $d\tau$ and the temperature gradient are related by Fourier law, according to which

$$dQ = -\lambda\, dF \operatorname{grad} t\, d\tau = -\lambda\, dF\, d\tau(\partial t/\partial n). \tag{22-6}$$

The minus sign in the right-hand side of Eq. (22-6) indicates that the temperature decreases in the direction of heat flow and that the quantity grad t is negative. The proportionality factor λ is referred to as the *thermal conductivity*. Equation (22-6) is known as the main equation of conduction, or Fourier law. The validity of Fourier law has been confirmed experimentally.

The quantity of heat passing through a unit area of isothermal surface per unit time is called the *rate of heat flow* and has dimension [W/m²]. The rate of heat flow

$$q = -\frac{dQ}{dF\, d\tau}, \quad \text{or} \quad q = -\lambda\left(\frac{\partial t}{\partial n}\right). \tag{22-7}$$

The vector of the rate of heat flow is normal to the isothermal surface in the direction of decreasing temperature. The vectors q and grad t lie on the same straight line but in opposite directions.

The quantity of heat passing per unit time through an arbitrary surface F is called the *heat flux*, having dimension [W]

$$Q = \int_F q\, dF = -\int_F \lambda\, dF\left(\frac{\partial t}{\partial n}\right). \tag{22-8}$$

The quantity of heat in joules flowing in time τ through an arbitrary surface F of finite size is determined by equation

$$Q = -\int_0^{\tau}\int_F \lambda\, dF\, d\tau\left(\frac{\partial t}{\partial n}\right). \tag{22-9}$$

Thus, to determine the quantity of heat flowing through any arbitrary surface of a solid, we must know the temperature field inside the body considered. The determination of the temperature field constitutes the fundamental problem in the analytical theory of heat transfer by conduction.

22-4. Thermal Conductivity

The coefficient of thermal conductivity λ is a physical property of a substance, which characterizes its ability to conduct heat. The dimension of thermal conductivity may be determined from Eq. (22-8)

$$\lambda = \frac{Q}{F(\partial t/\partial n)}.$$

The dimension of λ is $\dfrac{\text{W}}{\text{m}^2\cdot\text{deg/m}} = \text{W/m}\cdot\text{deg}$.

The numerical value of the thermal conductivity coefficient is the quantity of heat passing through unit area of an isothermal surface per unit time when the temperature gradient is unity (grad $t=1$). Thermal conductivity depends on pressure and temperature. The thermal conductivities of most substances are determined by experiment and are taken from reference tables for calculations.

Experimental studies have shown that for many materials the dependence of thermal conductivity on temperature can be assumed to be linear

$$\lambda=\lambda_0[1+b(t-t_0)],$$

where λ_0 = thermal conductivity at the temperature t_0 °C;
t = temperature, °C;
b = temperature coefficient (constant) determined by experiment.

The best conductors of heat are metals whose thermal conductivity λ varies from 3 to 458 W/m·deg. The thermal conductivities of pure metals, except aluminium, decrease with rising temperature. Heat is transported in metals mainly by free electrons. The most heat-conducting metal is pure silver ($\lambda=458$ W/m·deg).

The thermal conductivities of heat-insulating and building materials of a porous structure increase linearly with rising temperature and lie in the range 0.02-3.0 W/m·deg. The thermal conductivities of porous materials are greatly influenced by the gases filling the pores and have very small thermal conductivities compared with those of solid components. The increase in the thermal conductivity of porous materials with rising temperature is explained by the considerable increase in the intensity of radiation heat transfer between the surfaces of the solid "skeleton" of the pores through the air cells that separate them. The role of convection in the increase of thermal conductivity becomes more important with an increase in the size of the air-filled spaces in the material. That is why the effective coefficient of heat conductivity of a porous material has a complex nature and is a fictitious quantity. It is equal to the thermal conductivity of some homogeneous body of the same shape and size through which the same amount of heat is transferred under the given boundary temperature conditions.

Thermal conductivity is greatly influenced by the moisture content of substance. Experimental studies have shown that the thermal conductivity increases substantially with an increase in moisture content. In addition, the greater the volumetric density of a material, the fewer the pores in it, and the greater is its thermal conductivity.

The thermal conductivities of most liquids decrease with rising temperature; their values range from 0.08 to 0.65 W/m·deg. Water is an exception; when the temperature rises from 0° to 127 °C thermal conductivity increases, then diminishes with further increasing temperature. The thermal conductivity of liquids is practically independent of pressure.

The thermal conductivity of gases increases with rising temperature. Experimental studies have shown the thermal conductivity of gases to vary

TABLE 22-1

Material	ρ, kg/m³	t, °C	λ, W/m·deg	c, kJ/kg·deg	$a \times 10^6$, m²/s
Plate asbestos	770	30	0.1163	0.816	0.186
Asphalt (bitumen)	2 110	20	0.6978	2.09	0.156
Concrete	2 300	20	0.279	1.13	0.622
Refractory clay	1 850	450	1.035	1.089	0.051
Oak (across grain)	800	20	0.207	1.758	0.147
Wet earth	1 700	17	0.657	2.01	0.192
Coal	1 400	20	0.186	1.31	0.103
Red brick	1 800	0	0.768	0.879	—
Refractory brick	1 900	0	0.814	0.837	0.514
Ice	920	0	2.25	2.26	1.08
Mineral wool	200	50	0.0465	0.921	0.253
Boiler scale	1 000- -2 500	100	1.314- -3.14	—	—
Dry sand	1 500	20	0.326	0.795	2.74
Cork plate	200	27	0.0419	1.884	0.117
Hard rubber	1 200	0	0.169	1.382	0.098
Granulated sugar	1 600	0	0.582	1.256	0.278
Mica	290	20	0.582	0.879	2.28
Snow	560	—	0.465	2.09	0.4
Glass	2 500	20	0.744	0.67	0.444
Glass wool	200	0	0.037	0.67	0.278
Boiler slag	1 000	0	0.29	0.754	—
Slag wool	250	100	0.0698	—	—
Lime plaster	1 600	0	0.698	0.837	—
Aluminium	2 670	0	204	0.921	86.7
Brass	8 600	0	85	0.377	33.8
Copper	8 800	0	384	0.381	112.5
Nickel	9 000	20	58	0.461	17.8
Tin	7 230	0	64	0.221	41.1
Mercury	13 600	0	7.9	0.138	4.3
Lead	11 400	0	35	0.13	23.6
Silver	10 500	0	458	0.234	170
Carbon steel (C=0.5%)	7 900	20	45	0.461	14.7
Pig iron	7 220	20	63	0.502	17.0
Lamp black	165	40	0.166	—	—
Water	999.9	0	0.5513	4.212	0.131
Air (dry)	1.293	0	0.0244	1.005	18.8
Oxygen	1.429	0	0.0247	0.915	18.8
Nitrogen	1.25	0	0.0243	1.03	18.9
Hydrogen	0.0899	0	0.1721	14.192	135.0
Carbon oxide	1.25	0	0.0233	1.039	17.9

from 0.005 to 0.6 W/m·deg. The thermal conductivity of gases is practically independent of pressure.

For calculation purposes the numerical values of thermal conductivity and thermal diffusivity at different densities, temperatures and heat capacities are taken from reference tables (Table 22-1).

22-5. Differential Equation of Conduction

The study of any physical process is aimed at establishing the relationship between the quantities characterizing the given process. In complex processes, such as the process of heat transfer by conduction, we establish the relationship between these quantities by the methods of mathematical physics. These consider the development of a process not in the entire space investigated, but in the elementary volume of the substance in the course of an infinitesimal interval of time. The quantities associated with heat transfer by conduction are related by the *differential equations of conduction.* This makes it possible to ignore within the bounds of the elementary volume and the infinitesimal time interval selected, the variation of certain characteristic quantities of the process.

In deriving the differential equation of conduction, the following assumptions are made: there are no internal heat sources; the body considered is homogeneous and isotropic. Use is made of the law of conservation of energy which in the given case may be formulated as follows: "The difference between the quantity of heat transferred by conduction to the elementary parallelepiped during the time interval $d\tau$ and the quantity of heat leaving the elementary parallelepiped during the same time interval is expended in changing the internal energy of the parallelepiped".

Let us consider in a body an elementary parallelepiped with sides dx, dy, dz (Fig. 22-2). The sides are at different temperatures and so heat flows through the parallelepiped in the direction of the x-, y- and z-axes.

According to Fourier's law, the following quantity of heat passes through the area $dxdy$ during the time $d\tau$:

$$dQ_{z1} = -\lambda\, dx\, dy\, d\tau(\partial t/\partial z)$$

(grad t is taken in the form of a partial derivative, since temperature is assumed to depend not only on x, but also on the other coordinates and time).

The amount of heat leaving through the opposite side at a distance dz is determined from the expression

$$dQ_{z2} = -\lambda\, dx \cdot dy\, d\tau \frac{\partial}{\partial z}\left(t + \frac{\partial t}{\partial z}\, dz\right),$$

where $t + \frac{\partial t}{\partial z}\, dz$ is the temperature at the

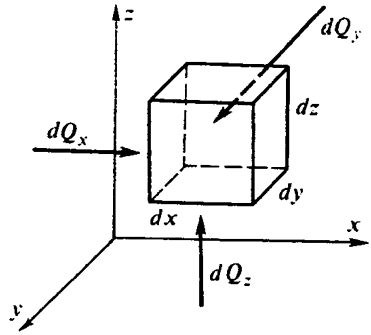


FIG. 22-2

second side, and the quantity $\frac{\partial t}{\partial z} dz$ represents variation of temperature in the z direction.

The above equation can be presented in another form

$$dQ_{z2} = -\lambda\, dx \cdot dy\, d\tau \left(\frac{\partial t}{\partial z}\right) - \lambda\, dx \cdot dy\, dz\, d\tau \left(\frac{\partial^2 t}{\partial z^2}\right).$$

The increase of internal energy in the parallelepiped in the direction of the z-axis is equal to

$$dQ_z = dQ_{z1} - dQ_{z2} = -\lambda\, dx \cdot dy\, d\tau \left(\frac{\partial t}{\partial z}\right) + \lambda\, dx \cdot dy\, d\tau \left(\frac{\partial t}{\partial z}\right) +$$

$$+ \lambda\, dx \cdot dy \cdot dz \cdot d\tau \left(\frac{\partial^2 t}{\partial z^2}\right),$$

or upon cancellation

$$dQ_z = \lambda\, dx \cdot dy \cdot dz\, d\tau \left(\frac{\partial^2 t}{\partial z^2}\right).$$

The increase of internal energy in the parallelepiped in the direction of the y-axis will be expressed by a similar equation

$$dQ_y = \lambda\, dx \cdot dy \cdot dz\, d\tau \left(\frac{\partial^2 t}{\partial y^2}\right),$$

and in the direction of the x-axis

$$dQ_x = \lambda\, dx \cdot dy \cdot dz\, d\tau \left(\frac{\partial^2 t}{\partial x^2}\right).$$

The total increase of internal energy in the parallelepiped is equal to

$$dQ = dQ_x + dQ_y + dQ_z = \lambda\, dx \cdot dy \cdot dz\, d\tau \left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right). \qquad \text{(a)}$$

On the other hand, in accordance with the law of conservation of energy

$$dQ = dx \cdot dy \cdot dz \varrho c \left(\frac{\partial t}{\partial \tau}\right) d\tau, \qquad \text{(b)}$$

where $dx \cdot dy \cdot dz$ = volume of parallelepiped considered;
$dx \cdot dy \cdot dz \varrho$ = mass of parallelepiped;
c = mass heat capacity;
$\left(\frac{\partial t}{\partial \tau}\right) d\tau$ = temparature variation with time

The left-hand sides of equations (a) and (b) are equal, therefore

$$\lambda\, dx \cdot dy \cdot dz\, d\tau \left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) = dx \cdot dy \cdot dz \varrho c \frac{\partial t}{\partial \tau} d\tau,$$

$$\frac{\partial t}{\partial \tau} = \frac{\lambda}{c\varrho}\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right).$$

The quantity $\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial z^2}\right)$ is called the *Laplace operator* and it is usually denoted by ∇^2 (∇ is read "nabla"); the quantity $\frac{\lambda}{c\varrho}$ is referred to as the *thermal diffusivity* and is denoted by the letter a. When these notations are used the differential equation of conduction acquires the following appearance:

$$\partial t/\partial \tau = a\,\nabla^2 t. \tag{22-10}$$

The differential equation of heat conduction (22-10) is also referred to as Fourier equation for a three-dimensional transient temperature field in the absence of internal heat sources. It is the basic equation used in the study of processes involving the heating and cooling of bodies in the course of heat transfer by conduction, and it gives the relationship between temporal and spatial variations of temperature at any point of the temperature field.

The thermal diffusivity $a=\frac{\lambda}{c\varrho}$ is a physical property of a substance and is measured in units of m^2/s. For transient processes of heat flow thermal diffusivity characterizes and defines the rate of change of temperature.

It follows from Eq. (22-10) that for any point of a body rate of change of temperature with time $\partial t/\partial \tau$ is proportional to a. Hence under the same conditions the rate of change in the temperature of a body is the higher, the larger its thermal diffusivity a. Gases have a small thermal diffusivity, and metals a large thermal diffusivity. The values of a for some materials are given in Table 22-1.

In the presence of heat sources the differential equation of conduction takes the following form

$$\frac{\partial t}{\partial \tau}=a\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right)+\frac{q_v}{c\varrho}, \tag{22-11}$$

where q_v = quantity of heat released in unit volume of substance per unit, W/m^3;
c = mass heat capacity of the body involved, J/kg·deg;
ϱ = density, kg/m^3.

In cylindrical coordinates, in the presence of internal heat sources, the differential equation reduces into

$$\frac{\partial t}{\partial \tau}=a\left(\frac{\partial^2 t}{\partial r^2}+\frac{1}{r}\frac{\partial t}{\partial r}+\frac{1}{r^2}\frac{\partial^2 t}{\partial \varphi^2}+\frac{\partial^2 t}{\partial z^2}\right)+\frac{q_v}{c\varrho}, \tag{22-12}$$

where r = radius-vector in the cylindrical system of coordinates,
φ = vectorial (polar) angle.

22-6. Boundary Conditions

The Fourier differential equation we have obtained describes the phenomenon of heat transfer by conduction in the most general form. In order to apply the equation to a particular process of conduction, it is necessary to know the distribution of temperatures inside the body at the initial instant of time, i.e. the initial conditions. In addition, the following must be known: the geometrical shape and size of the body, the physical parameters of the surrounding medium and the body itself, and the temperature distribution on the surface of the body, i.e. the interaction between the emitting body and the surrounding medium. All these constraints, combined with the differential equation of conduction, give a full description of the particular process of conduction, and they are referred to as the *uniqueness conditions* or *the boundary conditions.*

The initial conditions for temperature distribution are usually given for the moment of time $\tau=0$.

Boundary conditions may be given in three ways.

The boundary condition of the first kind gives the distribution of temperature on the surface of the body at any moment of time.

The boundary condition of the second kind gives the rate of heat flow for each point of the surface of the body for any moment of time.

The boundary condition of the third kind gives the ambient temperature and the law governing heat transfer between the surface of the body and its surroundings.

The laws governing heat transfer by convection between the surface of a body and its surroundings are very complex and they shall be considered in greater detail in a special chapter. The study of heat transfer by convection is based on Newton's law

$$q=\alpha(t_f-t_w), \tag{22-13}$$

where q = rate of heat flow, W/m²;
t_f = temperature of the surrounding medium (fluid), °C;
t_w = temperature of the surface (wall) of the body, °C;
α = coefficient of proportionality referred to as the *local heat-transfer coefficient*, W/m²·deg.

The local heat-transfer coefficient characterizes the intensity, or rate, of heat transfer between the surface of the body and the surrounding medium (fluid). It is numerically equal to the quantity of heat transferred from (or to) unit surface area per unit time where the temperature difference between the surface of the body and the surrounding medium is equal to 1°. The local heat-transfer coefficient depends on many factors, but when solving problems involving heat transfer in solids it is usually assumed constant.

In accordance with the law of conservation of energy, the quantity of heat lost from a unit surface area of the body to the surrounding medium per unit time, must be equal to the amount of heat that is transferred by con-

duction to the unit surface area per unit time from the interior of the body, i.e.

$$\alpha(t_w - t_f) = -\lambda\left(\frac{\partial t}{\partial n}\right)_{sur}, \tag{22-14}$$

where $\left(\frac{\partial t}{\partial n}\right)_{sur}$ is the projection of the temperature gradient on the direction of the normal to area dF; the subscript "*sur*" indicates that the temperature gradient pertains to the surface of the body (at $n=0$).

The equality (22-14) is the mathematical formulation, or description, of the condition of the third kind; it is valid for any moment of time.

With given uniqueness conditions a solution of the differential equation of conduction enables the determination of the temperature field over the entire volume of the body for any moment of time, i.e. it enables us to find the function

$$t = f(x, y, z, \tau).$$

Typical Questions to Chapter Twenty Two

1. Name the main cases of heat transfer by convection between a liquid or gas and the surface of a solid.
2. Describe in detail all cases of heat transfer by convection.
3. What is meant by heat transfer by convection?
4. What is the nature of radiant energy and of heat transfer by thermal radiation?
5. What gases are emitters?
6. What is meant by combined modes of heat transfer?
7. What is called a temperature field? Write down the equation of a temperature field.
8. Write down the equation of a steady-state temperature field.
9. Equation of a one-dimensional temperature field.
10. What is meant by the temperature gradient?
11. What is Fourier law?
12. What is meant by thermal conductivity?
13. Describe the peculiar features of the thermal conductivities of various substances.
14. Derive the differential equation of conduction.
15. Fourier equation for a three-dimensional temperature field.
16. What is called thermal diffusivity?
17. What quantities are given for the boundary conditions of the first, second and third kinds?
18. What is Newton's law?
19. What is meant by the local heat-transfer coefficient?

CHAPTER TWENTY THREE

STEADY-STATE CONDUCTION UNDER BOUNDARY CONDITIONS OF THE FIRST KIND

23-1. Heat Transfer Through a Single-Layer Plane Wall

The differential equation of conduction permits determination of temperature as functions of time and spatial coordinates at any point of the temperature field.

In any concrete case it is necessary to add to the equation the boundary conditions required.

Let us consider the most commonly encountered case of heat transfer by conduction through a single-layer plain wall, the length and width of which are infinitely large compared with the thickness δ (Fig. 23-1). The thickness of the wall is everywhere the same, with surface temperatures t'_w and t''_w being maintained constant, i.e. they are isothermal surfaces. The temperature varies only in the direction normal to the plane of the wall, and we assume this direction to be the x-axis. The thermal conductivity λ is assumed to be constant for the entire wall. With steady-state, or stationary, conditions of heat flow the temperature at any point of a body is constant and independent of time, i.e. $\partial t/\partial\tau=0$. Then, cancelling the thermal diffusivity, the differential equation of conduction takes the form

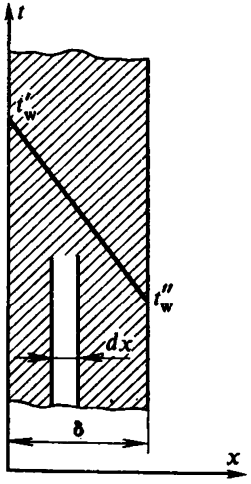


FIG. 23-1

$$\left(\frac{\partial^2 t}{\partial x^2}\right)+\left(\frac{\partial^2 t}{\partial y^2}\right)+\left(\frac{\partial^2 t}{\partial z^2}\right)=0.$$

But under the assumed conditions the first and second derivatives of t with respect to y and z are also equal to zero:

$$\frac{\partial t}{\partial y}=\frac{\partial t}{\partial z}=0 \quad \text{and} \quad \frac{\partial^2 t}{\partial y^2}=\frac{\partial^2 t}{\partial z^2}=0;$$

therefore the differential equation of conduction reduces into

$$\frac{\partial^2 t}{\partial x^2}=0. \tag{23-1}$$

Integrating Eq. (23-1), we find

$$\frac{dt}{dx}=\text{const}=A.$$

After a second integration, we obtain

$$t = Ax + B.$$

With a constant coefficient of thermal conductivity this is the equation of a straight line. Consequently, the law governing temperature variation when heat flows through a plain wall is *linear*.

Let us find the constants of integration A and B.

When $x=0$ temperature $t=t'_w=B$; when $x=\delta$ temperature $t=t''_w=A\delta+B=t'_w$, from which it follows that

$$A=\frac{t''_w-t'_w}{\delta}=\frac{dt}{dx}.$$

The rate of heat flow is found from Eq. (22-7)

$$q=-\lambda\left(\frac{\partial t}{\partial n}\right)=-\lambda\left(\frac{dt}{dx}\right)=-\lambda(t''_w-t'_w)/\delta$$

or

$$q=\frac{\lambda}{\delta}(t'_w-t''_w). \tag{23-2}$$

The ratio λ/δ is called heat conductivity.

Knowing the rate of heat flow, we can calculate the total quantity of heat that is transferred through wall surface F in time τ

$$Q=\frac{\lambda}{\delta}F(t'_w-t''_w)\tau. \tag{23-3}$$

The quantity of heat transferred by conduction through a plain wall is directly proportional to the thermal conductivity λ of the wall, its area F, the time interval τ, and the difference between outside surface temperatures, $t'_w-t''_w$, and it is inversely proportional to wall thickness δ. The total heat flux depends not on the absolute values of surface temperatures, but on their difference $t'_w-t''_w=\Delta t$, called the *temperature drop* or *temperature difference*.

The derived Eq. (23-2) is valid for the case when thermal conductivity is constant. Actually, the thermal conductivity of real bodies depends on the temperature and the graph depicting the temperature variation is a curved line. If in practice the thermal conductivity depends only slightly on the temperature, then the temperature variation graph is assumed to be linear.

Equation (23-2) can be derived directly from Fourier's law (22-6), assuming that temperature varies only in the direction of the x-axis

$$Q=-\lambda F\left(\frac{dt}{dx}\right).$$

Separating the variables, we obtain

$$dt=-\frac{Q}{\lambda F}dx.$$

Integrating the above equation assuming $Q=\text{const}$, we find that

$$t=-\frac{Q}{\lambda F}x+C.$$

The integration constant C can be found from the boundary conditions: when $x=0$, temperature $t=t'_w=C$;

when $x=\delta$, temperature $t=t''_w=-\frac{Q}{\lambda F}\delta+t'_w$, whence

$$Q=\frac{\lambda}{\delta}F(t'_w-t''_w).$$

Let us introduce into Eq. (23-2) corrections allowing for the dependence of λ on t, assuming this dependence to be linear

$$\lambda=\lambda_0(1+bt). \tag{a}$$

In this case, replacing the thermal conductivity λ in Fourier equation by its value from formula (a), we obtain

$$q=-\lambda(t)\frac{dt}{dx}=-\lambda_0(1+bt)\frac{dt}{dx}. \tag{b}$$

Separating the variables and integrating, we obtain

$$qx=-\lambda_0\left(t+\frac{bt^2}{2}\right)+C. \tag{c}$$

With boundary values of the variables we have:

$$\text{with } x=0, \quad t=t'_w \quad \text{and} \quad 0=-\lambda_0\left(t'_w+\frac{bt'^2_w}{2}\right)+C; \tag{d}$$

$$\text{with } x=\delta, \quad t=t''_w \quad \text{and} \quad q\delta=-\lambda_0\left(t''_w+\frac{bt''^2_w}{2}\right)+C. \tag{e}$$

Subtracting the first equality (d) from the second one (e), we find

$$q=\frac{\lambda_0}{\delta}\left[1+b\frac{t'_w+t''_w}{2}\right](t'_w-t''_w). \tag{23-4}$$

Equation (23-4) makes it possible to calculate the rate of heat flow with a variable thermal conductivity. In this equation the factor

$$\lambda_0\left(1+b\frac{t'_w+t''_w}{2}\right)$$

is the *integral mean value of thermal conductivity*.

In deriving Eq. (23-2) it was assumed that $\lambda=\text{const}$ and equal to the average thermal conductivity λ_{av}. Therefore, comparing Eqs. (23-2) and (23-4), we obtain

$$\lambda_{av}=\lambda_0\left(1+b\frac{t'_w-t''_w}{2}\right). \tag{23-5}$$

Consequently, when λ_{av} is determined at the integral mean temperature $t_{m\,w}=(t'_w+t''_w)/2$, formulae (23-2) and (23-4) are equivalent.

Then the rate of heat flow can be determined from equation

$$q=\frac{\lambda_{av}}{\delta}(t'_w-t''_w). \tag{23-6}$$

The equation of the curve representing temperature distribution in the wall is derived by solving the quadratic equation (c) with respect to t and substituting the value of C from equation (d)

$$t_x=\sqrt{\left(\frac{1}{b}+t'_w\right)^2-\frac{2qx}{\lambda_0 b}}-\frac{1}{b}. \tag{23-7}$$

It follows from Eq. (23-7) that inside the wall the temperature variation graph is curved. If the coefficient b is negative, the curve will be concave downward; if b is positive, the curve will be convex upward.

23-2. Heat Transfer by Conduction Through a Composite Plane Wall

Heat apparatuses often have walls consisting of several flat layers of different materials. Let us derive the equation of temperature distribution through such a wall, assuming the adjoining layers to be in close contact with each other.

The calculation formula for steady-state heat transfer by conduction in a composite wall can be derived from the equation of conduction for individual layers, assuming the rate of heat flow through any isothermal surface of the heterogeneous wall to be the same.

To solve this problem, let us consider a three-layer composite wall in which the thickness of individual layers is δ_1, δ_2, δ_3, and their thermal conductivities are respectively λ_1, λ_2, λ_3 (Fig. 23-2). The temperatures of the

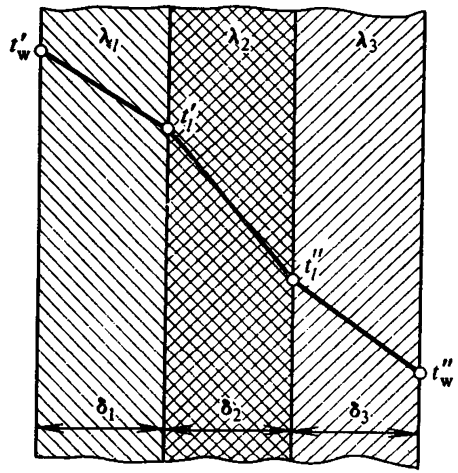


FIG. 23-2

external surfaces of the composite walls are t'_w and t''_w; the temperatures of the adjacent surfaces between the layers are denoted by t'_l and t''_l.

The heat flux for each layer is

$$Q=\frac{\lambda_1}{\delta_1}F(t'_w-t'_l); \quad Q=\frac{\lambda_2}{\delta_2}F(t'_l-t''_l);$$

$$Q=\frac{\lambda_3}{\delta_3}F(t''_l-t''_w).$$

Solving the above equations with respect to the temperature difference and adding, we obtain

$$t'_w-t'_l=\frac{Q}{F}\frac{\delta_1}{\lambda_1}; \quad t'_l-t''_l=\frac{Q}{F}\frac{\delta_2}{\lambda_2};$$

$$t''_l-t''_w=\frac{Q}{F}\frac{\delta_3}{\lambda_3}; \quad t'_w-t''_w=\frac{Q}{F}\left(\frac{\delta_1}{\lambda_1}+\frac{\delta_2}{\lambda_2}+\frac{\delta_3}{\lambda_3}\right),$$

whence

$$Q=\frac{F(t'_w-t''_w)}{\frac{\delta_1}{\lambda_1}+\frac{\delta_2}{\lambda_2}+\frac{\delta_3}{\lambda_3}} \tag{23-8}$$

or for n layers

$$Q=\frac{F(t'_w-t''_w)}{\sum\limits_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}} \tag{23-9}$$

The ratio $\frac{\delta}{\lambda}$ is called the *internal thermal resistance of a layer*, and the quantity $\sum\limits_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}$ is referred to as the *overall internal thermal resistance* to heat flow through a composite wall.

Heat flow through a plain composite wall is sometimes calculated, assuming the wall to be homogeneous and introducing into Eq. (23-9) the equivalent thermal conductivity λ_{eq}

$$Q=\frac{\lambda_{eq}F(t'_w-t''_w)}{\sum\limits_{i=1}^{i=n}\delta_i} \tag{23-10}$$

Comparing Eqs. (23-9) and (23-10), we obtain

$$\lambda_{eq}=\frac{\sum\limits_{i=1}^{i=n}\delta_i}{\sum\limits_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}} \tag{23-11}$$

The equivalent thermal conductivity of a composite wall is equal to the thermal conductivity of a homogeneous wall of the same thickness and the same surface temperatures and through which a similar heat flux flows.

The magnitude of the equivalent thermal conductivity depends on the thermal resistance to heat flow and the thickness of the individual layers.

The interface temperatures, deg C, between any two adjacent layers of a composite wall are equal to

$$\left.\begin{aligned} t_1' &= t_w' - \frac{Q}{F}\frac{\delta_1}{\lambda_1}; \\ t_1'' &= t_1' - \frac{Q}{F}\frac{\delta_2}{\lambda_2}; \\ t_1''' &= t_1'' - \frac{Q}{F}\frac{\delta_3}{\lambda_3}, \text{ etc.} \end{aligned}\right\} \qquad (23\text{-}12)$$

With a constant thermal conductivity the temperature variation graph in each layer of the composite wall is linear, and the temperature graph of a composite multi-layer plane wall is a broken line.

23-3. Heat Transfer by Conduction Through a Single-Layer Cylindrical Wall

The outside and inside surfaces of a plane cylindrical tube are maintained at constant temperatures t_w' and t_w''. The isothermal surfaces are cylindrical surfaces having a common axis with the tube. Temperature varies only with the radius, so that heat flux also flows in the radial direction. The tube is considered to be of infinite length. The temperature field is then of the one-dimensional kind

$$t = f(r),$$

where r is the current cylindrical coordinate.

When the temperature distribution on the surfaces of the tube is non-uniform, the temperature field will not be one-dimensional and the above equation will not be valid.

In the tube shown in Fig. 23-3 heat flows radially. Consider a section of the tube of length l. The surface F at a distance r from the axis is equal to $2\pi rl$. The temperature of the inside surface is t_w' and of the outside—t_w''. The rate of heat flow through the two surfaces is the same.

Let us consider an annular layer inside the wall with radius r and thickness dr. Then the surfaces through which heat flows can be assumed to be the same and this elementary layer considered as a plane wall. The difference between the temperatures of these surfaces shall also be infinitely small and equal to dt. By Fourier's law

$$Q = -\lambda F l \frac{dt}{dr},$$

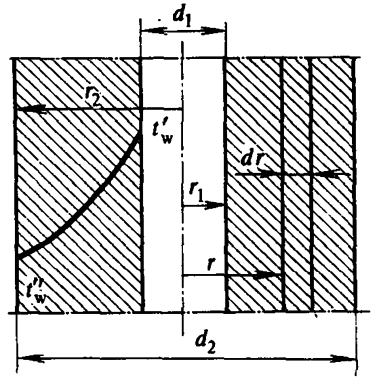


FIG. 23-3

or for the annular layer

$$Q=-\lambda 2\pi rl\frac{dt}{dr}.$$

Separating the variables, we obtain

$$dt=-\frac{Q}{2\pi\lambda l}\frac{dr}{r}. \tag{a}$$

Integrating Eq. (a) between the limits from t'_w to t''_w and from r_1 to r_2 at $\lambda=\text{const}$, we obtain

$$\int_{t'_w}^{t''_w} dt=-\int_{r_1}^{r_2}\frac{Q}{2\pi\lambda l}\frac{dr}{r},$$

$$t'_w-t''_w=\frac{Q}{2\pi\lambda l}\ln\frac{r_2}{r_1},$$

whence

$$Q=\frac{l(t'_w-t''_w)}{\frac{1}{2\pi\lambda}\ln\frac{d_2}{d_1}}. \tag{23-13}$$

It is clear from Eq. (23-13) that temperature distribution in the wall of a cylindrical tube is represented by a logarithmic curve. The heat flux passing through the cylindrical wall is determined by the given boundary conditions and depends on the ratio of the outside diameter of the tube to its inside diameter.

The heat flux can be reduced to unit length of the tube, q_l, and to 1 m^2 of the inside or outside surface, q_1 and q_2. Then the calculation equations take the following form:

$$q_l=\frac{Q}{l}=\frac{2\pi\lambda(t'_w-t''_w)}{\ln\frac{d_2}{d_1}} \tag{23-14}$$

$$q_1=\frac{Q}{\pi d_1 l}=\frac{2\lambda(t'_w-t''_w)}{d_1\ln\frac{d_2}{d_1}} \tag{23-15}$$

$$q_2=\frac{Q}{\pi d_2 l}=\frac{2\lambda(t'_w-t''_w)}{d_2\ln\frac{d_2}{d_1}} \tag{23-16}$$

23-4. Heat Transfer by Conduction Through a Multi-Layer Composite Cylindrical Wall

Let us assume that the cylindrical wall consists of three layers in close contact with each other. The temperature of the inside surface is t'_w and of the outside—t''_w; the thermal conductivities of the layers are λ_1, λ_2 and

λ_3; the diameters of the layers are d_1, d_2, d_3 and d_4. The temperature of each layer of the composite wall varies according to logarithmic curve. The overall profile of temperature variation is represented by a sectional logarithmic curve. Under steady-state conditions the rate of heat flow is the same for all layers. The heat flux through each layer is

$$Q=\frac{2\pi\lambda_1 l(t'_w-t'_l)}{\ln\frac{d_2}{d_1}};$$

$$Q=\frac{2\pi\lambda_2 l(t'_l-t''_l)}{\ln\frac{d_3}{d_2}};$$

$$Q=\frac{2\pi\lambda_3 l(t''_l-t''_w)}{\ln\frac{d_4}{d_3}}$$

Solving the obtained equations for the temperature differences and adding up, we obtain

$$+\begin{cases} t'_w-t'_l=\dfrac{Q}{2\pi\lambda_1 l}\ln\dfrac{d_2}{d_1} \\ t'_l-t''_l=\dfrac{Q}{2\pi\lambda_2 l}\ln\dfrac{d_3}{d_2} \\ t''_l-t''_w=\dfrac{Q}{2\pi\lambda_3 l}\ln\dfrac{d_4}{d_3} \end{cases}$$

$$t'_w-t''_w=\frac{Q}{2\pi l}\left(\frac{1}{\lambda_1}\ln\frac{d_2}{d_1}+\frac{1}{\lambda_2}\ln\frac{d_3}{d_2}+\frac{1}{\lambda_3}\ln\frac{d_4}{d_3}\right)$$

whence

$$Q=\frac{2\pi l(t'_w-t''_w)}{\frac{1}{\lambda_1}\ln\frac{d_2}{d_1}+\frac{1}{\lambda_2}\ln\frac{d_3}{d_2}+\frac{1}{\lambda_3}\ln\frac{d_4}{d_3}}. \qquad (23\text{-}17)$$

For a multi-layer composite cylindrical wall with n layers

$$Q=\frac{2\pi l(t'_w-t''_w)}{\sum\limits_{i=1}^{i=n}\frac{1}{\lambda_i}\ln\frac{d_{i+1}}{d_i}}. \qquad (23\text{-}18)$$

Introducing into the calculation formula for the heat flux, Eq. (23-18), the equivalent thermal conductivity, we get

$$Q=\frac{2\pi\lambda_{eq}(t'_w-t''_w)}{\Sigma\ln\frac{d_{i+1}}{d_i}} \qquad (23\text{-}19)$$

The equivalent thermal conductivity for a cylindrical wall is determined in the same way as for a plain wall. A comparison of Eqs. (23-18) and (23-19) yields

$$\lambda_{eq}=\frac{\frac{\Sigma \ln d_{i+1}}{d_i}}{\sum_{i=1}^{i=n}\frac{1}{\lambda_i}\ln\frac{d_{i+1}}{d_i}}. \tag{23-20}$$

The interface temperatures between layers are found by means of the following equation

$$\left.\begin{aligned} t_l'&=t_w'-\frac{Q}{2\pi\lambda_1 l}\ln\frac{d_2}{d_1}\\ t_l''&=t_l'-\frac{Q}{2\pi\lambda_2 l}\ln\frac{d_3}{d_2}\ \text{ etc.}\end{aligned}\right\} \tag{23-21}$$

23-5. Heat Transfer by Conduction Through a Spherical Wall

A constant heat flux is directed through a spherical wall with the heat source being located inside the sphere. Temperature varies only in the radial direction. The isothermal surfaces are concentric spherical surfaces. The temperature of the inside surface is t_w' and the temperature of the outside—t_w''; the thermal conductivity λ of the wall is constant. The inner and outer radii of the sphere are r_1 and r_2.

The heat flux passing through a spherical layer with radius r and thickness dr is found from Fourier equation

$$Q=-\lambda F\frac{dt}{dr}=-\lambda 4\pi r^2\frac{dt}{dr},$$

or

$$dt=-\frac{Q}{4\pi\lambda}\frac{dr}{r^2}.$$

Integrating the above equation with respect to t and r, and determining the integration constant from the boundary conditions stating that at $r=r_1$, $t=t_w'$; at $r=r_2$, $t=t_w''$, we obtain

$$Q=\frac{4\pi\lambda(t_w'-t_w'')}{\frac{1}{r_1}-\frac{1}{r_2}}=\frac{2\pi\lambda(t_w'-t_w'')}{\frac{1}{d_1}-\frac{1}{d_2}}. \tag{23-22}$$

23-6. Heat Transfer by Conduction Through Bodies of Arbitrary Shape

It follows from the preceding sections that for each shape of a body there exists a definite calculation formula for heat transfer by conduction and it is not advisable to apply these equations to bodies (or solids) of irregular shape.

The heat flux passing through the walls of bodies of irregular shape (for instance when the wall is not plane and its boundary surfaces are curvilinear, or when the surface is not cylindrical but oval) can be determined by the following equation:

$$Q=\frac{\lambda}{\delta}F_m(t'_w-t''_w), \tag{23-23}$$

where F_m is the surface, found depending on the shape of the body.

For a plane and cylindrical walls with $\frac{F_2}{F_1}<2$ (where F_1 is the inside surface of the solid and F_2—the outside surface)

$$F_m=\frac{F_1+F_2}{2}. \tag{23-24}$$

For a cylindrical wall with $\frac{F_2}{F_1}>2$

$$F_m=\frac{F_2-F_1}{2.3\log F_2/F_1}. \tag{23-25}$$

For a spherical wall

$$F_m=\sqrt{F_1F_2}. \tag{23-26}$$

All the above formulae are suitable for approximate calculations.

When dealing with complex solids heat transfer by conduction is usually calculated for individual component parts of the solids, but this method is only of an approximate nature. Reliable data on the conduction of complex solids can only be obtained experimentally.

If temperature differs at individual points of a wall, it is necessary to find the average calculation formula for the entire wall, making use of the following formula:

$$t_m=\frac{F_1t_1+F_2t_2+\ldots+F_nt_n}{F_1+F_2+\ldots+F_n},$$

where $F_1, F_2, \ldots, F_n$ = sections of the wall at a constant temperature;
$t_1, t_2, \ldots, t_n$ = temperatures of individual sections.

Typical Questions and Examples to Chapter Twenty Three

1. Write down the differential equation of conduction through a single-layer plane wall.
2. Derive the equation of heat conduction through a single-layer plane wall.
3. What law governs temperature variation in a plane wall?
4. What quantities influence the heat flux by conduction through a single-layer plane wall?
5. Conduction through a composite plane wall—derivation of the equation of heat conduction.

6. What is meant by equivalent coefficient of thermal conductivity?
7. How is the interface temperature between adjoining layers of a composite wall determined?
8. Equation of the temperature field for a cylindrical wall.
9. Conduction through a plain cylindrical wall—derivation of the equation of heat conduction.
10. What law governs temperature variation in a cylindrical wall?
11. What quantities influence heat transfer by conduction through a single-layer cylindrical wall?
12. Derive the equation of conduction through a composite cylindrical wall.
13. The equivalent coefficient of thermal conductivity for a cylindrical wall.
14. How are the interface temperatures between neighbouring layers of a composite cylindrical wall determined?
15. Conduction through a spherical wall—derivation of the equation.

Example 23-1. Determine the heat flux through a brick wall 5 m high, 4 m wide and 250 mm thick. The wall surface temperature $t'_w=27$ °C and $t''_w=-23$ °C. The thermal conductivity of brick is 0.77 W/m·deg.

The heat flux is determined by Eq. (23-3)

$$Q=\frac{\lambda}{\delta}F(t'_w-t''_w)=\frac{0.77}{0.25}\times 5\times 4[27-(-23)]=3080 \text{ W}.$$

Example 23-2. Determine the difference between the inside and outside surface temperatures of the steel wall of a boiler operated at a gauge pressure of 19 bar. The boiler wall is 20 mm thick; boiler feedwater temperature is 46 °C. Boiler capacity is 25 kg/h of saturated dry steam per 1 m² of heating surface. The thermal conductivity of steel $\lambda=50$ W/m·deg. Barometric pressure is equal to 750 mm Hg. The boiler wall is assumed to be planar.

The absolute pressure in the boiler

$$p_{abs}=p_p+p_{bar}=19+\frac{750}{750}=20 \text{ bar}.$$

At the absolute boiler pressure of 20 bar the enthalpy of dry saturated steam is $i''=2799.2$ kJ/kg.

At the temperature of 46 °C the enthalpy of boiler feedwater, $i'=192$ kJ/kg, is taken from Tables I or II (Appendix).

The rate of heat flow through the wall

$$q=(2799.2-192)25=65\,200 \text{ kJ/m}^2\cdot\text{h}.$$

The magnitude of the temperature difference Δt can be found from the main equation of conduction

$$\Delta t=\frac{\delta}{\lambda}q=\frac{0.02\times 65\,200\,000}{50\times 3600}\approx 7 \text{ °C}.$$

Example 23-3. Calculate the rate of heat flow through the wall of a boiler furnace not covered with waterwall tubes. The wall is 625 mm thick, built-up of three layers: one layer of refractory brick 250 mm thick; an isolating interlayer of small-piece slag 125 mm thick, and a layer of red brick 250 mm thick. The temperature of the inside surface of the furnace wall $t'_w = 1527$ °C, and the outside surface is at a temperature $t''_w = 47$ °C. The thermal conductivities of refractory brick $\lambda_1 = 1.28$ W/m·deg, of the isolating interlayer, $\lambda_2 = 0.15$ W/m·deg, and of the red brick $\lambda_3 = 0.8$ W/m·deg. How shall the rate of heat flow through the furnace wall change, if the insulating interlayer is replaced with red brick? Determine the percentage saving due to the use of the insulating interlayer. In addition, determine the interface temperatures between layers.

The rate of heat flow through a multilayer composite wall is determined by Eq. (23-8)

$$q = \frac{Q}{F} = \frac{t'_w - t''_w}{\frac{\delta_1}{\lambda_1} + \frac{\delta_2}{\lambda_2} + \frac{\delta_3}{\lambda_3}} = \frac{1527 - 47}{\frac{0.25}{1.28} + \frac{0.125}{0.15} + \frac{0.25}{0.8}} = \frac{1480}{1.341} = 1100 \text{ W/m}^2.$$

If the insulating interlayer is replaced by red brick

$$q = \frac{Q}{F} = \frac{1527 - 47}{\frac{0.25}{1.28} + \frac{0.375}{0.8}} = \frac{1480}{0.663} = 2230 \text{ W/m}^2.$$

The percentage saving due to the insulating interlayer is

$$\frac{(2230 - 1100) \times 100}{2230} = 50.7 \text{ per cent.}$$

The temperature between the chamotte brick and the insulating interlayer is determined by formula (23-12)

$$t'_l = t'_w - \frac{q\delta_1}{\lambda_1} = 1527 - \frac{1100 \times 0.25}{1.28} = 1312 \text{ °C.}$$

The temperature between the insulating interlayer and red brick

$$t''_l = t'_l - \frac{q\delta_2}{\lambda_2} = 1312 - \frac{1100 \times 0.125}{0.15} = 400 \text{ °C.}$$

The temperature between the chamotte and red brick

$$t'_l = 1527 - \frac{2230 \times 0.25}{1.28} = 1091 \text{ °C.}$$

As can be seen from the calculation, the insulating interlayer not only diminishes heat losses, but also preserves the red brick wall. At temperatures above 900 °C red brick deteriorates rapidly.

Example 23-4. A flat steel wall whose thermal conductivity $\lambda_1 = 50$ W/m·deg and thickness $\delta_1 = 0.02$ m is insulated from heat losses by a layer of asbestos cardboard with a thermal conductivity $\lambda_2 = 0.15$ W/m·deg and

thickness $\delta_2=0.2$ m and a layer of cork with a thermal conductivity $\lambda_3=0.045$ W/m·deg and thickness $\delta_3=0.1$ m. What should the thickness be of a layer of foam concrete with a thermal conductivity $\lambda=0.08$ W/m·deg, replacing the asbestos and cork, for the heat-insulating properties of the wall to remain the same? The equivalent thermal conductivity of the three-layer composite wall is determined from Eq. (23-11)

$$\lambda_{eq}=\frac{\delta_1+\delta_2+\delta_3}{\frac{\delta_1}{\lambda_1}+\frac{\delta_2}{\lambda_2}+\frac{\delta_3}{\lambda_3}}=\frac{0.02+0.2+0.1}{\frac{0.02}{50}+\frac{0.2}{0.15}+\frac{0.1}{0.045}}=\frac{0.32}{3.556}=0.092 \text{ W/m·deg.}$$

With the same heat losses the equivalent thermal conductivity of the new insulation remains equal to that of the composite wall, therefore

$$0.092=\frac{0.02+x}{\frac{0.02}{50}+\frac{x}{0.08}}, \quad \text{whence } x=0.133 \text{ m}$$

Example 23-5. A steel tube with diameters $\frac{d_1}{d_2}=\frac{200}{220}$ mm and a thermal conductivity $\lambda_1=50$ W/m·deg is covered with two layers of insulating material. The thickness of the first layer is $\delta_2=50$ mm and of the second layer is $\delta_3=80$ mm while the thermal conductivity of the first layer $\lambda_2=0.2$ W/m·deg and thermal conductivity of the second layer $\lambda_3=0.1$ W/m·deg. The temperature of the tube inner surface $t'_w=327$ °C and of the outer surface of the insulation $t''_w=45$ °C. Determine the heat losses through the insulation for a length of 1 m of the pipeline and also the interface temperatures between the individual layers.

Given are $d_1=0.2$ m, $d_2=0.22$ m, $d_3=0.32$ m and $d_4=0.48$ m.

In accordance with Eq. (23-17), we obtain

$$q_l=\frac{Q}{l}=\frac{2\pi(t'_w-t''_w)}{\frac{1}{\lambda_1}\ln\frac{d_2}{d_1}+\frac{1}{\lambda_2}\ln\frac{d_3}{d_2}+\frac{1}{\lambda_3}\ln\frac{d_4}{d_3}}=$$

$$=\frac{2\times3.14(327-47)}{2.3\left(\frac{1}{50}\log\frac{0.22}{0.2}+\frac{1}{0.2}\log\frac{0.32}{0.22}+\frac{1}{0.1}\log\frac{0.48}{0.32}\right)}=282 \text{ W/m}^2.$$

The interface temperature between layers is found from Eq. (23-21)

$$t'_l=t'_w-\frac{q_l}{2\pi\lambda_1}\ln\frac{d_2}{d_1}=327-\frac{282\times2.3}{2\times3.14\times50}\log\frac{0.22}{0.2}=327-0.087\cong327 \text{ °C.}$$

$$t''_l=t'_l-\frac{q_l}{2\pi\lambda_2}\ln\frac{d_3}{d_2}=327-\frac{282\times2.3}{2\times3.14\times0.2}\log\frac{0.32}{0.22}=327-84=243 \text{ °C.}$$

CHAPTER TWENTY FOUR

STEADY-STATE CONDUCTION WITH BOUNDARY CONDITIONS OF THE THIRD KIND. HEAT-TRANSFER COEFFICIENT

24-1. Heat Transfer Through Plane and Composite Walls

The transport of heat from one moving medium (hot) to another (cold) through a single or multilayer plane wall of any shape is referred to as *heat transfer.*

Examples of heat transfer are: the transfer of heat from the heating water to the air in a room through the walls of the heating radiator of a district-heating system, the transfer of heat from the flue gases to water through the walls of generating tubes in steam boilers, the transfer of heat from the condensing vapour to cooling water through the walls of condenser tubes, the transfer of heat from hot gases to the cooling water through the wall of a cylinder of an internal combustion engine, etc. In all the examples cited above the wall serves as a conductor of heat and is made from a material with a high thermal conductivity.

In other applications, where the loss of heat should be reduced, the wall must serve as an insulator and be made from a material with good heat-insulating properties. Walls are encountered in a variety of forms: flat or finned plates, banks of cylindrical, finned or studded tubes, and also spherical surfaces, etc.

Heat transfer is rather a complex process in which all the modes of heat transfer are involved: conduction, convection and thermal radiation.

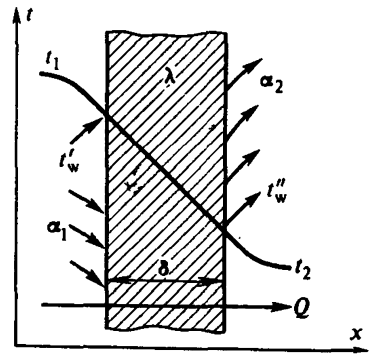


FIG. 24-1

In fact, in the presence of a separating wall, the process of heat transfer is the combination of three stages (Fig. 24-1). The first stage involves heat transfer by convection from the hot heat-carrier to the wall. Convection is always accompanied by conduction and often—by thermal radiation. The second stage is heat transfer by conduction through the wall. When heat propagation takes place in porous solids conduction is associated with convection and radiation in the pores. The third link involves heat transfer by convection from the opposite surface of the separating wall to a cold heat-carrying agent. Here, convection is also accompanied by conduction and often by thermal radiation.

The quantity of heat transferred from the hot heat-carrying agent to the wall by convection is determined by Newton's equation

$$Q=\alpha_1 F(t_1-t'_w), \tag{24-1}$$

where α_1 = local coefficient of heat transfer from the hot heat-carrying agent at a constant temperature t_1 to the external surface of the plane separating wall, accounting for all the modes of heat transfer;

F = calculation surface (area) of the separating wall, m².

The flux of heat transferred by conduction through the plane wall is determined by equation

$$Q=\frac{\lambda}{\delta}F(t'_w-t''_w). \tag{24-2}$$

The quantity of heat transferred from the second surface of the separating wall to the cold heat-carrying agent is also determined from Newton's equation

$$Q=\alpha_2 F(t''_w-t_2), \tag{24-3}$$

where α_2 is the local coefficient of heat transfer from the second wall surface to the cold heat-carrying agent at the constant temperature t_2.

The quantities Q in equations (24-1), (24-2) and (24-3) are the same. The quantity of heat taken up by the wall under steady-state conditions is equal to the quantity leaving it.

Solving the three heat-transfer equations with respect to the temperature differences, we have

$$\left.\begin{aligned} t_1-t'_w&=\frac{Q}{\alpha_1 F},\\ t'_w-t''_w&=\frac{\delta}{\lambda}\frac{Q}{F},\\ t''_w-t_2&=\frac{Q}{\alpha_2 F}. \end{aligned}\right\}+$$

Adding up the equalities obtained, we get

$$Q=\frac{F(t_1-t_2)}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}} \tag{24-4}$$

or the rate of heat flow is equal to

$$q=\frac{t_1-t_2}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}}.$$

In equation (24-4) the quantity $\frac{1}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}}$ is denoted by the letter k,

measured in units of W/m²·deg, and referred to as the *overall heat-transfer coefficient*

$$k=\frac{1}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}} \tag{24-5}$$

then,

$$Q=kF(t_1-t_2)$$

or

$$q=k(t_1-t_2). \tag{24-6}$$

The numerical value of the overall heat-transfer coefficient represents the quantity of heat passing through unit area of separating wall surface from a high-temperature to a low-temperature heat-carrying agent at a temperature difference of 1 °C.

The derived equation (24-6) is called the *equation of heat transfer* from one fluid to another through a separating wall.

To determine the overall heat-transfer coefficient k it is first necessary to identify α_1 and α_2 which usually are complicated quantities; they account for combined heat transfer by convection and thermal radiation

$$\alpha=\alpha_{con}+\alpha_{rad}.$$

The magnitude of k is always less than the smallest α.

The reciprocal of the overall heat-transfer coefficient,

$$R=\frac{1}{k}=\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}, \tag{24-7}$$

is called the *overall thermal resistance* to heat flow through a single-layer plane wall. This quantity is measured in units of m²·deg/W. The ratios $\frac{1}{\alpha_1}$ and $\frac{1}{\alpha_2}$ represent the external thermal resistances to heat flow; the ratio $\frac{\delta}{\lambda}$ is the internal thermal resistance to heat flow through the wall.

In applications where heat is transferred through a multilayer plane wall the denominator in formula (24-4) must be the sum of the thermal resistances to heat flow of all the layers

$$Q=\frac{F(t_1-t_2)}{\frac{1}{\alpha_1}+\sum_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}+\frac{1}{\alpha_2}}, \tag{24-8}$$

$$q=\frac{Q}{F}=\frac{t_1-t_2}{\frac{1}{\alpha_1}+\sum_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}+\frac{1}{\alpha_2}}$$

The overall coefficient of heat transfer through a multilayer plane wall, k, is equal to

$$k=\frac{1}{\frac{1}{\alpha_1}+\sum_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}+\frac{1}{\alpha_2}} \tag{24-9}$$

The overall thermal resistance to heat flow through a multilayer plane wall

$$R=\frac{1}{k}=\frac{1}{\alpha_1}+\sum_{i=1}^{i=n}\frac{\delta_i}{\lambda_i}+\frac{1}{\alpha_2}.$$

The surface temperatures of a plane wall are determined from the following equations

$$\left.\begin{aligned} t'_w&=t_1-\frac{Q}{\alpha_1 F},\\ t''_w&=t_2+\frac{Q}{\alpha_2 F}\end{aligned}\right\} \tag{24-10}$$

With known α and k, the surface temperatures of a plane wall can be determined from the following formulae:

$$\begin{aligned} &\alpha_1(t_1-t'_w)=k(t_1-t_2),\\ &\alpha_2(t''_w-t_2)=k(t_1-t_2),\\ &t'_w=t_1-\frac{k}{\alpha_1}(t_1-t_2),\\ &t''_w=t_2+\frac{k}{\alpha_2}(t_1-t_2).\end{aligned} \tag{24-11}$$

24-2. Heat Transfer Through Single-Layer and Multi-Layer Walls of a Cylinder

Let us assume that steady-state heat transfer takes place at a cylindrical homogeneous wall from a hot heat-carrying agent at a constant temperature t_1 and with a local heat-transfer coefficient α_1 to a cold heat-carrying agent at a constant temperature t_2, having a local heat-transfer coefficient α_2 (Fig. 24-2).

Then, three equations can be written for the heat flux

$$Q=\alpha_1\pi d_{in}l(t_1-t'_w);\quad Q=\frac{\pi l}{\frac{1}{2\lambda}\ln\frac{d_{out}}{d_{in}}}(t'_w-t''_w);$$

$$Q=\alpha_2\pi d_{out}l(t''_w-t_2).$$

Solving these three equations with respect to the temperature difference, then adding up, we obtain

$$Q=\frac{\pi l(t_1-t_2)}{\frac{1}{\alpha_1 d_{in}}+\frac{1}{2\lambda}\ln\frac{d_{out}}{d_{in}}+\frac{1}{\alpha_2 d_{out}}} \tag{24-12}$$

where

$$\frac{1}{\frac{1}{\alpha_1 d_{in}}+\frac{1}{2\lambda}\ln\frac{d_{out}}{d_{in}}+\frac{1}{\alpha_2 d_{out}}}=k_{cyl} \qquad (24\text{-}13)$$

is referred to as the *linear overall heat-transfer coefficient*, measured in units of W/m·deg.

The rate of heat flow through a cylindrical wall is equal to

$$q_{cyl}=\frac{Q}{l}=k_{cyl}\pi(t_1-t_2).$$

The numerical value of the linear overall coefficient of heat transfer through a cylindrical wall, k_{cyl}, is equal to the quantity of heat passing through 1 m length of a tube per unit time from a high-temperature heat-carrying agent to a low-temperature heat-carrying agent at a temperature difference of 1 °C.

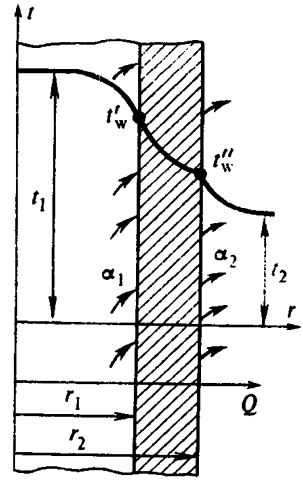


FIG. 24-2

It follows from this that Eq. (24-12) can take the form

$$Q=k_{cyl}\pi l(t_1-t_2). \qquad (24\text{-}14)$$

When heat is transferred through a multilayer cylindrical wall built-up of n layers, the heat flux is equal to

$$Q=\frac{\pi l(t_1-t_2)}{\frac{1}{\alpha_1 d_{in}}+\sum_{i=1}^{i=n}\frac{1}{2\lambda_i}\ln\frac{d_{i+1}}{d_i}+\frac{1}{\alpha_2 d_{out}}}. \qquad (24\text{-}15)$$

The rate of heat flow reduced to the inner or outer surfaces of the cylindrical wall is determined from equations

$$q_{cyl\,1}=\frac{Q}{\pi d_1 l}=\frac{k_{cyl}}{d_1}(t_1-t_2);$$

$$q_{cyl\,2}=\frac{Q}{\pi d_2 l}=\frac{k_{cyl}}{d_2}(t_1-t_2).$$

The reciprocal of the linear overall coefficient of heat transfer, $\frac{1}{k_{cyl}}$, is called the *linear overall thermal resistance* to heat flow through a cylindrical wall.

$$R_{cyl}=\frac{1}{k_{cyl}}=\frac{1}{\alpha_1 d_{in}}+\sum_{i=1}^{i=n}\frac{1}{2\lambda_i}\ln\frac{d_{i+1}}{d_i}+\frac{1}{\alpha_2 d_{out}} \qquad (24\text{-}16)$$

where $\frac{1}{\alpha_1 d_{in}}$ and $\frac{1}{\alpha_2 d_{out}}$ = external thermal resistances to heat flow;

$\sum_{i=1}^{i=n}\frac{1}{2\lambda_i}\ln\frac{d_{i+1}}{d_i}$ = internal thermal resistance to heat flow of a composite cylindrical wall.

The dimension of R_{cyl} is m·deg/W.

The temperature of the inner surface in °C is determined by formula

$$t'_w = t_1 - \frac{Q}{\alpha_1 d_{in} \pi l}, \tag{24-17}$$

and the temperature of the outer surface

$$t''_w = t_2 + \frac{Q}{\alpha_2 d_{out} \pi l}. \tag{24-18}$$

24-3. Critical Diameter of Insulation

By *heat insulation* is meant any coating on a hot surface that reduces the loss of heat to the surroundings by thermal radiation. For heat insulation any materials having a low thermal conductivity may be used such as asbestos, cork, mica, slag or glass wool, wool, sawdust, peat, etc.

The formula for the linear overall thermal resistance to heat flow through a cylindrical wall shows that the heat losses from insulated pipelines decrease with increasing thickness of the insulating material used.

Let us see how conditions under which the material used to insulate a tube reduces heat losses to the surroundings.

Let a cylindrical tube be coated with a single-layer of insulating material. With α_1, α_2, d_1, d_2, λ_1, λ_2, t_1 and t_2 constant, let us see how the overall thermal resistance to heat flow changes with a change in the thickness of the insulation.

It can be seen from the equation of the overall thermal resistance of a double-layer cylindrical wall

$$R_{cyl} = \frac{1}{k_{cyl}} = \frac{1}{\alpha_1 d_1} + \frac{1}{2\lambda_1} \ln \frac{d_2}{d_1} + \frac{1}{2\lambda_2} \ln \frac{d_3}{d_2} + \frac{1}{\alpha_2 d_3},$$

that an increase of the outer diameter of the insulation d_3 causes an increase in the thermal resistance of the layer of insulation $\left(\text{the term } \frac{1}{2\lambda_1} \ln \frac{d_3}{d_2}\right)$ but simultaneously the resistance to heat transfer from the outer surface of the insulation diminishes $\left(\text{term } \frac{1}{\alpha_2 d_3}\right)$.

Taking the first derivative of the right-hand side of the equation with respect to d_3 and equating it to zero, we obtain

$$\frac{d(R_{cyl})}{d(d_3)} = \frac{1}{2\lambda_2 d_3} - \frac{1}{\alpha_2 d_3^2} = 0.$$

Then the critical diameter of insulation corresponding to the extremal point of the curve $R = f(d_3)$ will be determined by formula

$$d_{cr} = d_{ins} = \frac{2\lambda_{2ins}}{\alpha_2}. \tag{24-19}$$

It follows from Eq. (24-19) that the critical diameter of insulation, d_{cr}, does not depend on pipeline dimensions. It decreases if the thermal con-

ductivity of the insulation is reduced while it increases if the local coefficient of heat transfer, α_2, from the outside surface of the insulation to the surrounding medium is increased.

The second derivative of R_{cyl} is greater than zero. Consequently, the critical diameter corresponds to the minimum resistance to heat flow and the maximum heat flux (Fig. 24-3).

Equation (24-19) shows that if the outer diameter of the insulation, d_{ins}, increases, but remains less than d_{cr}, the heat losses increase and exceed the losses of heat from a bare pipeline (curve AK). When $d_{ins}=d_{cr}$ the heat losses to the surrounding medium are maximum (point K). With a further increase of the outer diameter of the insulation, $d_{ins}>d_{cr}$, the heat losses are smaller than when $d_{ins}=d_{cr}$ (curve BK).

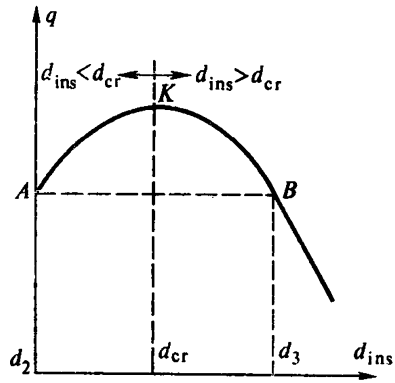


FIG. 24-3

Only when $d_{ins}=d_3$ are the heat losses equal to those of a bare, non-insulated, pipeline.

This means that to be effective, heat insulation must have a critical diameter which is smaller than the outer diameter of the non-insulated pipeline, i.e. d_{cr} must be smaller than or equal to d_3 (Fig. 24-3). Thus, for the insulation to reduce the loss of heat from a cylindrical wall, compared with a non-insulated pipeline, with a given outer tube diameter d_2, and a given heat-transfer coefficient α_2, it is necessary that

$$\lambda_{ins} \leqslant \frac{\alpha_2 d_2}{2}.$$

For instance, suppose slag wool with a thermal conductivity $\lambda_{ins}=0.1$ W/m·deg is available for the insulation of a pipeline having a diameter $d_2=30$ mm; the local heat-transfer coefficient $\alpha_2=4.0$ W/m²·deg. Is it worthwhile to use the slag wool for insulating material?

The critical diameter of the insulation

$$d_{cr}=\frac{2\lambda_{ins}}{\alpha_2}=\frac{2\times 0.1}{4}=0.05 \text{ m}=50 \text{ mm}.$$

Since $d_{cr}>d_2$, it is not worthwhile to use the slag wool in the case considered.

For the insulation to be effective, the thermal conductivity of the material must be smaller:

$$\lambda_{ins} \leqslant \frac{4\times 0.03}{2}=0.06 \text{ W/m·deg}.$$

24-4. Heat Transfer Through a Spherical Wall

The boundary conditions of the third kind for a hollow sphere are as follows: the inner diameter is d_1 and the outer diameter d_2; the hot heat-carrying agent inside the sphere has temperature t_1, and the cold heat-carrying agent has temperature t_2; the coefficient of heat transfer from the hot liquid to the inner surface of the sphere is α_1, and the coefficient of heat transfer from the outer surface to the surrounding medium is α_2.

Under steady-state conditions for all isothermal surfaces the heat flux will be constant:

$$Q=\alpha_1\pi d_1^2(t_1-t_w'); \quad Q=\frac{2\pi\lambda}{\frac{1}{d_1}-\frac{1}{d_2}}(t_w'-t_w'');$$

$$Q=\alpha_2\pi d_2^2(t_w''-t_2).$$

Solving these three equations for the temperature differences and adding up, we find the heat flux

$$Q=\frac{\pi(t_1-t_2)}{\frac{1}{\alpha_1 d_1^2}+\frac{1}{2\lambda}\left(\frac{1}{d_1}-\frac{1}{d_2}\right)+\frac{1}{\alpha_2 d_2^2}}$$

or

$$Q=k_{sph}\pi(t_1-t_2). \tag{24-20}$$

From Eq. (24-20) we determine the overall coefficient of heat transfer through a spherical wall

$$k_{sph}=\frac{1}{\frac{1}{\alpha_1 d_1^2}+\frac{1}{2\lambda}\left(\frac{1}{d_1}-\frac{1}{d_2}\right)+\frac{1}{\alpha_2 d_2^2}}. \tag{24-21}$$

The dimension of k_{sph} is W/deg.

The reciprocal of k_{sph}

$$\frac{1}{k_{sph}}=\frac{1}{\alpha_1 d_1^2}+\frac{1}{2\lambda}\left(\frac{1}{d_1}-\frac{1}{d_2}\right)+\frac{1}{\alpha_2 d_2^2}$$

is called the *overall thermal resistance* of a spherical wall.

24-5. Heat Transfer Through a Finned Wall

Finned, or extended, surfaces are used to balance the thermal resistances of heat transfer on both sides of a wall, when one wall surface is exposed to a liquid with a large local heat-transfer coefficient, and the other surface is exposed to a gas having a small heat-transfer coefficient, creating a high thermal resistance.

The finning of a wall with a high thermal resistance makes it possible to increase the surface exposed to the high- (or low)-temperature fluid, to diminish the overall thermal resistance and to increase the heat flux.

The temperature on a fin varies with height if $t_1 > t_2$; at the base of a fin it is equal to the wall surface temperature t'_w, and the temperature at the top of a fin is lower than t''_w. That is why the sections of the surface of a fin at the base transfer more heat than the sections of the fin at the top. The ratio of the quantity of heat Q_f transferred from the surface of a fin to the surrounding medium to the amount of heat Q_{sf} that this surface would be capable of transferring at a constant temperature equal to that at the base of the fins, is referred to as the *fin efficiency*

$$\eta_e = \frac{Q_f}{Q_{sf}}$$

The fin efficiency is always less than unity. For short fins made from a material with a high thermal conductivity the fin efficiency is close to unity.

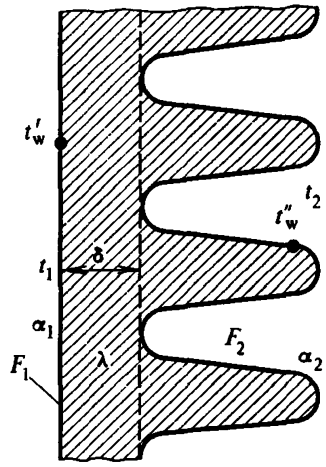


FIG. 24-4

Consider a plane wall with a thickness δ one side of which is finned (Fig. 24-4). The temperature of the plane surface of the fins and of the surfaces between them is assumed as a first approximation to be constant and equal to t''_w. The wall and the fins are made of the same material with high thermal conductivity λ. The local heat-transfer coefficient on the plane side of the wall is α_1 and on the finned side—α_2^*. The area of the plane surface is F_1, the area of the fins and the spaces between them is F_2. The temperature of the hot heat-carrying agent is t_1 and of the cold—t_2. Then, for steady-state heat flow we can write the following three equations for the heat flux

$$Q = \alpha_1 F_1 (t_1 - t'_w), \quad Q = \frac{\lambda}{\delta} F_1 (t'_w - t''_w), \quad Q = \alpha_2 F_2 (t'_w - t_2).$$

Solving these three equations with respect to the temperature difference and adding up, we obtain

$$Q = \frac{t_1 - t_2}{\frac{1}{\alpha_1 F_1} + \frac{\delta}{\lambda F_1} + \frac{1}{\alpha_2 F_2}},$$

or

$$Q = k_f (t_1 - t_2), \tag{24-22}$$

* The local heat-transfer coefficient α_2 for finned surfaces is usually referred to as the reduced coefficient, since it accounts for heat transfer from the surfaces of the tube and fins, and also the fin efficiency.

whence the overall coefficient of heat transfer through a finned wall

$$k_f = \frac{1}{\frac{1}{\alpha_1 F_1} + \frac{\delta}{\lambda F_1} + \frac{1}{\alpha_2 F_2}}. \tag{24-23}$$

The dimension of k_f is W/deg.

If the heat flux is reduced to unit plane surface, then

$$k_{fp} = \frac{1}{\frac{1}{\alpha_1} + \frac{\delta}{\lambda} + \frac{1}{\alpha_2}\frac{F_1}{F_2}} \tag{24-24}$$

The coefficient k_{fp} is measured in units of W/m²·deg.

If the heat flux is reduced to unit finned surface, then

$$k_{ff} = \frac{1}{\frac{1}{\alpha_1}\frac{F_2}{F_1} + \frac{\delta}{\lambda}\frac{F_2}{F_1} + \frac{1}{\alpha_2}} \tag{24-25}$$

For a round externally finned tube we obtain by analogy

$$Q = k_{fr}(t_1 - t_2), \tag{24-26}$$

whence

$$k_{fr} = \frac{1}{\frac{1}{\alpha_1 d_1} + \frac{1}{2\lambda}\ln\frac{d_2}{d_1} + \frac{1}{\alpha_2 d_2}\frac{F_2}{F_1}} \tag{24-27}$$

where d_1 = inside diameter of tube;
d_2 = outside diameter of tube.

The coefficient k_{kr} is measured in units of W/m·deg.

The above formulae are valid for fins of a small height.

The ratio of the finned surface F_2 to the plane one F_1 is called the *fin factor*. The effect of finning on the heat transfer coefficient is considered in example 24-5.

The exact magnitude of the coefficient of heat transfer through finned surfaces can only be determined experimentally [4].

24-6. Intensification of Heat Transfer

The experience gained in the practical operation of heat apparatus has shown it necessary to provide the best conditions for the transfer of heat from a high-temperature heat-carrying agent to a low-temperature heat-carrying agent. These conditions mainly depend on the heat transfer coefficient. However, the knowledge of the numerical value of the heat transfer coefficient alone is insufficient for investigating heat transfer processes. Only an analysis of the interrelationships amongst all thermal

resistances to heat flow makes it possible to draw a correct conclusion and to change significantly the rate of heat flow. This can be illustrated by considering some examples.

In a steam boiler the coefficient of heat transfer from the flue gas to the wall $\alpha_1 = 30$ W/m²·deg, and from the wall to the boiling water—$\alpha_2 = 5000$ W/m²·deg; the thermal conductivity of the steel wall $\lambda = 50$ W/m·deg, and wall thickness $\delta = 0.02$ m. The wall is assumed to be plain (flat). Under the conditions given the overall heat transfer coefficient $k = 29.5$ W/m²·deg, i.e. it is smaller than the smallest local heat-transfer coefficient α.

The attempt to increase the overall heat transfer coefficient k, by either improving the conditions under which heat is transferred from the wall to the water, or by using a thinner wall made from a heat-conducting material proves to be unsuccessful. The coefficient can be increased appreciably only by improving the heat transfer from the flue gases to the wall.

The situation is different with apparatus in which the local heat-transfer coefficients α_1 and α_2 are large. In a water condenser, for instance, on the water side $\alpha_1 = 5000$ W/m²·deg and on the steam side, $\alpha_2 = 10\,000$ W/m²·deg. If the wall of such a condenser is made from 20 mm thick steel plate then $k = 1428$ W/m²·deg, and for a wall 3 mm thick $k = 2770$ W/m²·deg; and if the steel wall is replaced with a copper one 1 mm thick then $k = 3400$ W/m²·deg. The example considered indicates that when the local heat-transfer coefficients are large the overall heat-transfer coefficient depends to a great extent on the thermal conductivity of the separating wall.

Thus, heat transfer in heat apparatus can be intensified by trying to reduce the largest thermal resistances.

Typical Questions and Examples to Chapter Twenty Four

1. What is meant by heat transfer?
2. Describe heat transfer through a wall.
3. What equation describes heat transfer through a wall?
4. How is the main heat-transfer equation derived?
5. What is meant by the overall heat-transfer coefficient?
6. What is meant by the overall thermal resistance to heat flow and what are its component quantities?
7. Heat transfer through a plane composite wall and the overall heat-transfer coefficient for such a wall.
8. How are the surface temperatures of a wall determined?
9. Derive the heat-transfer equation for heat transfer through a plane single-layer cylindrical wall.
10. Give a definition of the coefficient of heat transfer through a single-layer cylindrical wall.
11. What is meant by the heat flux and the coefficient of heat transfer through a multilayer composite cylindrical wall.
12. Derive the equation for the overall thermal resistance to heat flow through a multilayer composite cylindrical wall.

13. How are the inner and outer surface temperatures of a cylindrical wall determined?
14. What is meant by the critical thickness of insulation?
15. What is meant by the critical diameter of insulation and how is it determined?
16. What conditions must be observed for the insulation to reduce the heat losses?
17. Heat transfer through a spherical wall; derivation of the heat-transfer equation.
18. Overall heat-transfer coefficient and overall thermal resistance to heat flow through a spherical wall.
19. When are finned walls used?
20. Heat transfer and the coefficient of heat transfer through a finned wall.
21. In which cases and how can heat transfer be intensified?
22. What is the general rule to be followed when measures are taken to intensify heat transfer?

Example 24-1. Determine the rate of heat flow through a plain steel wall with a thickness $\delta=10$ mm and thermal conductivity $\lambda=50$ W/m·deg, and also the overall heat-transfer coefficients k for two cases. (1). Flue gas temperature $t_1=1127$ °C, boiling water temperature $t_2=227$ °C, the local coefficient of heat transfer from the flue gas to the wall $\alpha_1=100$ W/m²·deg, and from the wall to the boiling water $\alpha_2=5000$ W/m²·deg. (2). In the course of service, the heating surface became covered on the gas side with a layer of soot of a thickness $\delta=2$ mm. The thermal conductivity of soot $\lambda=0.09$ W/m·deg. The temperatures of the flue gases and boiling water remain unchanged.

Calculate the interface temperatures between the layers and also determine how many times the heat-transfer coefficient decreases due to the soot deposit on the heating surface.

First case. The overall heat-transfer coefficient is determined by formula (24-5)

$$k=\frac{1}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}}=\frac{1}{\frac{1}{100}+\frac{0.01}{50}+\frac{1}{5000}}=96.2 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow is determined by Eq. (24-6)

$$q=k(t_1-t_2)=96.2(1127-227)=86\,600 \text{ W/m}^2=86.6 \text{ kW/m}^2.$$

The surface temperature of the wall on the flue gas side is determined by formula (24-10)

$$t_w'=t_1-\frac{q}{\alpha_1}=1127-\frac{86\,600}{100}=261 \text{ °C}.$$

The surface temperature of the wall on the water side is

$$t_w''=t_2+\frac{q}{\alpha_2}=227+\frac{86\,600}{5000}=244.3 \text{ °C}.$$

Second case. The overall coefficient of heat transfer through a plane composite wall is determined by formula (24-9)

$$k=\frac{1}{\frac{1}{\alpha_1}+\frac{\delta_1}{\lambda_1}+\frac{\delta_2}{\lambda_2}+\frac{1}{\alpha_2}}=\frac{1}{\frac{1}{100}+\frac{0.002}{0.09}+\frac{0.01}{50}+\frac{1}{5000}}=30.7 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow is found by formula (24-8)

$$q=k(t_1-t_2)=30.7(1127-227)=27\,600 \text{ W/m}^2.$$

The outer surface temperature of the layer of soot is

$$t'_w=1127-\frac{27\,600}{100}=851 \text{ °C}.$$

The inner surface temperature of the layer of soot is

$$t'_l=t'_w-\frac{q\delta_1}{\lambda_1}=851-\frac{27\,600\times0.002}{0.09}=238 \text{ °C}.$$

The surface temperature of the wall on the water side is

$$t''_w=227+\frac{27\,600}{5000}=232.5 \text{ °C}.$$

The layer of soot 2 mm thick diminishes the overall coefficient of heat transfer from the flue gases to the water 3.13 times.

Example 24-2. How do the rate of heat flow and the surface temperature of the wall change, if under the conditions of Example 24-1 a layer of scale 10 mm thick forms on the water side? The thermal conductivity of scale is $\lambda=2.0$ W/m·deg. On the flue gas side the surface of the wall is not contaminated.

Solve the problem if the layer is 30 mm thick under the same conditions.

With a layer of scale 10 mm thick the overall heat-transfer coefficient is equal to

$$k=\frac{1}{\frac{1}{100}+\frac{0.01}{50}+\frac{0.01}{2}+\frac{1}{5000}}=65.0 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow amounts to

$$q=65(1127-227)=58\,500 \text{ W/m}^2.$$

The interface temperatures between the layers are equal to

$$t'_w=1127-\frac{58\,500}{100}=542 \text{ °C};$$

$$t'_l=542-\frac{58\,500\times0.01}{50}=530 \text{ °C};$$

$$t''_w=227+\frac{58\,500}{5000}=239 \text{ °C}.$$

With a layer of scale 30 mm thick the overall heat-transfer coefficient is equal to

$$k=\frac{1}{\frac{1}{100}+\frac{0.01}{50}+\frac{0.03}{2}+\frac{1}{5000}}=39.4 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow is equal to

$$q=39.4(1127-227)=35\,600 \text{ W/m}^2.$$

The surface and interface temperatures are as follows:

$$t'_w=1127-\frac{35\,600}{100}=771 \text{ °C};$$

$$t'_l=771-\frac{35\,600\times0.01}{50}=764 \text{ °C};$$

$$t''_w=227+\frac{35\,600}{5000}=234 \text{ °C}.$$

The calculations indicate that the depositing of scale on the heating surface reduces the rate of heat transfer. A layer of scale 10 mm thick reduces the rate by 32.4 per cent; a layer 30 mm thick reduces it by 59 per cent. In addition, the calculations show that the temperature of the steel wall increases sharply with the appearance of scale and reaches 771 °C when the layer of scale is 30 mm, which is absolutely inadmissible. The deposition of a thick layer of scale may lead to boiler explosion.

Example 24-3. A steel pipeline with diameter ratio $\frac{d_1}{d_2}=180/200$ mm and thermal conductivity $\lambda_1=50$ W/m·deg is covered with a layer of heat-resistant insulation 50 mm thick; the thermal conductivity of the insulating material is $\lambda_2=0.18$ W/m·deg. The insulation is topped with a layer of cork 50 mm thick, $\lambda_3=0.06$ W/m·deg. The temperature of the steam carried by the pipeline is $t_1=427$ °C, and the ambient air temperature $t_2=27$ °C. The local coefficient of heat transfer from the steam to the tube is $\alpha_1=200$ W/m²·deg and the coefficient of heat transfer from the surface of the cork insulation to the surrounding air $\alpha_2=10$ W/m²·deg. Determine the loss of heat from a 1 m length of the pipeline, and also the surface temperature of individual layers.

The overall coefficient of heat transfer through a composite cylindrical wall is determined by Eq. (24-13):

$$k_{cyl}=\frac{1}{\frac{1}{\alpha_1 d_{in}}+\frac{1}{2\lambda_1}\ln\frac{d_1}{d_{in}}+\frac{1}{2\lambda_2}\ln\frac{d_2}{d_1}+\frac{1}{2\lambda_3}\ln\frac{d_3}{d_2}+\frac{1}{\alpha_2 d_{out}}}=$$

$$=\frac{1}{\frac{1}{200\times0.18}+\frac{2.3}{2\times50}\log\frac{200}{180}+\frac{2.3}{2\times0.18}\log\frac{300}{200}+\frac{2.3}{2\times0.06}\log\frac{400}{300}+\frac{1}{10\times0.4}}=$$

$$=0.263 \text{ W/m}\cdot\text{deg}.$$

The rate of heat flow per 1 m of tube length

$$q=k_{cyl}\pi(t_1-t_2)=0.263\times3.14(427-27)=330 \text{ W/m}.$$

The inner surface temperature of the tube is determined by Eq. (24-17)

$$t'_w=t_1-\frac{q}{\alpha_1 d_{in}\pi}=427-\frac{330}{200\times0.18\times3.14}=424 \text{ °C}.$$

The thermal resistance to heat flow of the steel tube can be ignored and its outer surface temperature assumed equal to $t'_l=424$ °C.

The outer surface temperature of the heat-resistant insulation is determined by Eq. (23-21)

$$t''_l=t'_l-\frac{q}{2\pi\lambda_2}\ln\frac{d_2}{d_1}=424-\frac{300\times2.3\times0.176}{2\times3.14\times0.18}=306 \text{ °C}.$$

The outer surface temperature of the cork insulation is determined by Eq. (24-18)

$$t''_w=t_2+\frac{q}{\alpha_2 d_{out}\pi}=27+\frac{330}{10\times0.4\times3.14}=53.3 \text{ °C}.$$

The foregoing calculations show that the layer of the heat-resistant insulation is too thin and fails to protect the cork from self-ignition, since the maximum admissible temperature for cork is 80 °C. Hence, the thickness of the heat-resistant layer of insulation must be increased.

Example 24-4. Determine the quantity of heat lost from a spherical evaporating apparatus whose inside diameter is $d_1=1.5$ m, and whose outside diameter (together with the insulation) $d_2=2.0$ m. The average thermal conductivity of the wall $\lambda_{av}=0.12$ W/m·deg. The temperature of the working medium inside the sphere $t_1=127$ °C, ambient air temperature $t_2=27$ °C. The local heat-transfer coefficient $\alpha_1=200$ W/m²·deg and $\alpha_2=8$ W/m²·deg.

The overall coefficient of heat transfer through the spherical wall of the apparatus is determined by Eq. (24-21)

$$k_{sph}=\frac{1}{\frac{1}{\alpha_1 d_1^2}+\frac{1}{2\lambda_{av}}\left(\frac{1}{d_1}-\frac{1}{d_2}\right)+\frac{1}{\lambda_2 d_2^2}}=\frac{1}{\frac{1}{200\times1.5^2}+\frac{1}{2\times0.12}\left(\frac{1}{1.5}-\frac{1}{2.0}\right)+\frac{1}{8\times2^2}}=$$

$$=1.38 \text{ W/m}^2\cdot\text{deg}.$$

We find the amount of heat lost from the apparatus to the surroundings from Eq. (24-20)

$$Q=k_{sph}\pi(t_1-t_2)=1.38\times3.14(127-27)=434 \text{ W}.$$

Example 24-5. Determine the quantity of heat transferred through 1 m² of a finned wall whose finning factor is $\frac{F_2}{F_1}=12$. The wall is fabricated from iron with a thermal conductivity $\lambda=63$ W/m·deg and wall thickness $\delta=12$ mm. The coefficient of heat transfer from the working medium to the

wall $\alpha_1=250$ W/m²·deg and $\alpha_2=12$ W/m²·deg. The temperature of the working medium $t_1=117$ °C and ambient air temperature $t_2=17$ °C.

The overall heat-transfer coefficient is determined by formula (24-24) and we assume the rate of heat flow to be related to a plane surface

$$k_{fp}=\frac{1}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}\frac{F_1}{F_2}}=\frac{1}{\frac{1}{250}+\frac{0.012}{63}+\frac{1}{12\times12}}=90 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow is determined from Eq. (24-22):

$$q=k_{fp}(t_1-t_2)=90(117-17)=9000 \text{ W/m}^2.$$

With a plane wall surface k is determined by Eq. (24-5)

$$k=\frac{1}{\frac{1}{250}+\frac{0.012}{63}+\frac{1}{12}}=11.4 \text{ W/m}^2\cdot\text{deg}.$$

The rate of heat flow through a plane wall amounts to

$$q=11.4\times100=1140 \text{ W/m}^2.$$

Finning of the surface increases the rate of heat transfer 7.9 times. In reality, when account is taken of the variation of the heat-transfer coefficient and temperature along the fins, finning may be considerably less effective.

CHAPTER TWENTY FIVE

TRANSIENT CONDUCTION

25-1. Basic Concepts

All processes occurring when the temperature field varies with time are referred to as *transient.*

Transient or non-stationary conduction takes place in the cooling of metal blanks, in the calcination (roasting) of solids, in the process of glass manufacture, in brick firing, in the heating of wood, in the rubber vulcanization, in heating of flour in sacks, etc.

Transient, or non-stationary, conductive heat transfer can be determined by finding the relationships governing the variation of the temperature field and heat flux in time and in space

$$f=f(x,\ y,\ z,\ \tau) \quad \text{and} \quad Q=\varphi(x,\ y,\ z,\ \tau),$$

where $x,\ y,\ z$ = the coordinates of a point;
τ = time.

The indicated relationships can be found by solving Fourier differential equation of heat conduction

$$\frac{\partial t}{\partial \tau}=a\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right)=a\,\nabla^2 t. \tag{25-1}$$

In solving Eq. (25-1), the boundary conditions and the initial temperature distribution in the body must be given.

Boundary conditions are given by the equation

$$\left(\frac{\partial t}{\partial n}\right)_{surf}=-\left(\frac{\alpha}{\lambda_w}\right)(t_{surf}-t_{sur}), \tag{25-2}$$

where $\left(\frac{\partial t}{\partial n}\right)_{surf}$ = temperature gradient on the surface;
α = coefficient of heat transfer between a fluid and the surface of a solid;
λ_w = thermal conductivity of the wall;
t_{surf} = wall surface temperature;
t_{sur} = temperature of surrounding medium.

The physical quantities λ, c, ϱ are assumed constant.

At the initial moment of time at $\tau=0$ the temperature distribution in the body is considered to be uniform, i.e.

$t_0=\text{const}$.

Solving Eqs. (25-1) and (25-2) with account taken of the boundary and time conditions, we obtain the following equation of the temperature field

$$t=f(\alpha, \lambda, a, \tau, x, y, z, t_0, t_m, l_0, l_1, \ldots, l_n). \tag{25-3}$$

It can be seen from Eq. (25-3) that temperature depends on a great number of variables and constant parameters and its solution involves a rather complex mathematical problem that cannot be treated in a brief textbook.

A detailed treatment of the solutions can be found in special courses of heat transfer. That is why we shall restrict ourselves in the following to the presentation of formulae already derived for three problems: the cooling or heating of an infinite plate; the cooling or heating of an infinite cylinder and the cooling or heating of a sphere.

An analysis of Eq. (25-3) shows it possible to group the variables in three dimensionless terms

$\frac{\alpha l}{\lambda_w}$ = Bi, the Biot number;

$\frac{a\tau}{l^2}$ = Fo, the Fourier number;

$\frac{x}{l}$ — a dimensionless coordinate.

The unknown function in the form of dimensionless temperature $\frac{\vartheta^*}{\vartheta_1}$ can be represented by the following equation:

$$\frac{\vartheta}{\vartheta_1}=F\left(\text{Fo}, \text{Bi}, \frac{x}{l}\right). \tag{25-4}$$

25-2. Infinite Plate

Let us consider the cooling of a plane-parallel plate of thickness 2δ ($l=\delta$). The dimensions of the plate in the direction of the Oy- and Oz-axes are infinitely large (Fig. 25-1). The plate is exposed to a liquid or gas at a constant temperature t_m on all sides, with the two local coefficients of heat transfer α being identical and constant for the two surfaces.

At the initial moment of time all points of the plate have the same temperature, t_0, therefore the excess temperature $\vartheta_1=t_0-t_m$ shall also be the same for all points on the surface of the plate. In addition, the thermal conductivity λ_w, density of the plate ϱ and its heat capacity c are given and all these quantities are assumed to be constant. The temperature diffusivity a is determined from equation $a=\lambda/c\varrho$. Since the plate is of infinite width and length, the differential equation of conduction takes the form

$$\frac{\partial\vartheta}{\alpha\tau}=a\frac{\alpha^2\theta}{\partial x^2}.$$

* Here and in the following the quantity ϑ denotes the excess temperature of a body above ambient temperature, i.e. $\vartheta=t_b-t_{sur}$.

The boundary condition at $x=\pm\delta$ is

$$\left(\frac{\partial\vartheta}{\partial x}\right)_{x=\pm\delta}=\pm\frac{\alpha\vartheta_w}{\lambda_w}$$

and the initial condition at $\tau=0$

$$\vartheta=\vartheta_1.$$

The surface temperatures of the wall (plate) and the temperature in the middle plane of the wall are determined from the relationship

$$\frac{\vartheta_w}{\vartheta_1}=\frac{t_w-t_m}{t_0-t_m}=f\left(\frac{\alpha l}{\lambda_w},\ \frac{a\tau}{l^2}\right)=f(\text{Bi},\ \text{Fo}) \qquad (25\text{-}5)$$

In the average plane and on the surfaces of the plate the dimensional coordinate x/l becomes constant (at $x=0$ $x/l=0$; at $x=\delta$ $x/l=1$) and so is not present in Eq. (25-5):

$$\frac{\vartheta_{av}}{\vartheta_1}=\frac{t_{av}-t_m}{t_0+t_m}=f_1(\text{Bi},\ \text{Fo}). \qquad (25\text{-}6)$$

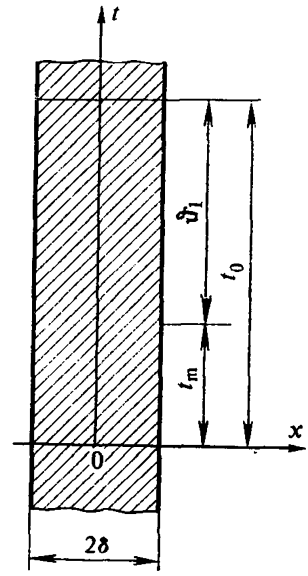


FIG. 25-1

The amount of heat transferred from (or to) the plate to (or from) the surrounding medium in time τ must be equal to the change in its internal energy during the period of its complete cooling (heating).

The initial internal energy of the plate, measured from the internal energy at the temperature of the surrounding medium, taken to be zero, is equal to

$$Q_0=2Fc\varrho\delta(t_0-t_m)=2Fc\varrho\delta\vartheta_1. \qquad (25\text{-}7)$$

The quantity of heat released upon cooling of the plate is also determined by the dimensional terms Bi and Fo

$$\frac{Q_\tau}{Q_0}=f_2(\text{Bi},\ \text{Fo}), \qquad (25\text{-}8)$$

$$Q_\tau=F2c\varrho\delta(t_0-t_{m\,w}),$$

where Q_τ = quantity of heat transferred to the surrounding medium during the time interval τ, J;

$t_{m\,w}$ = mean temperature of the plate upon the elapse of time τ, °C

The relationships (25-5), (25-6) and (25-8) are presented graphically in Figures 25-2, 25-3 and 25-4. First the Bi and Fo numbers are calculated, then the charts are used to determine $\vartheta_{av}/\vartheta_1$, ϑ_w/ϑ_1, Q_τ/Q_0. Since $t_0=t_m$ and the initial enthalpy are known, it is easy to calculate t_w, t_{av} and Q_τ.

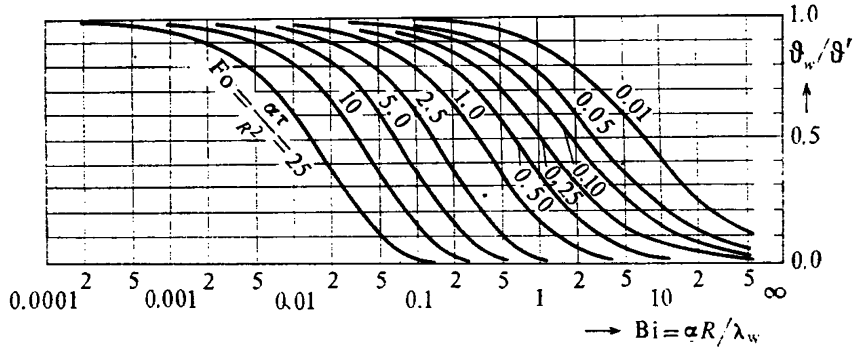


FIG. 25-2

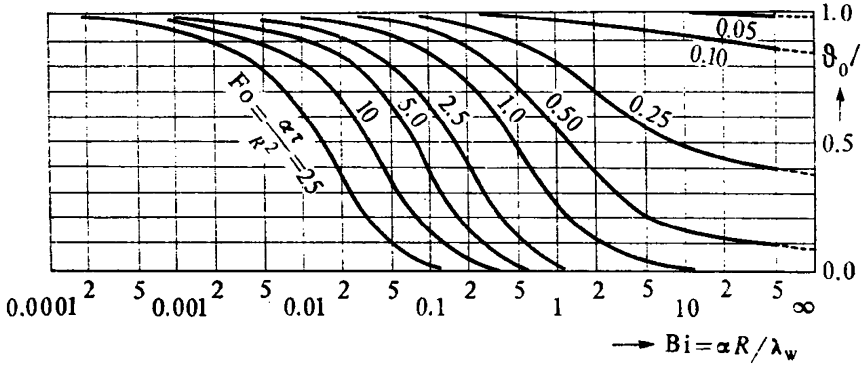


FIG. 25-3

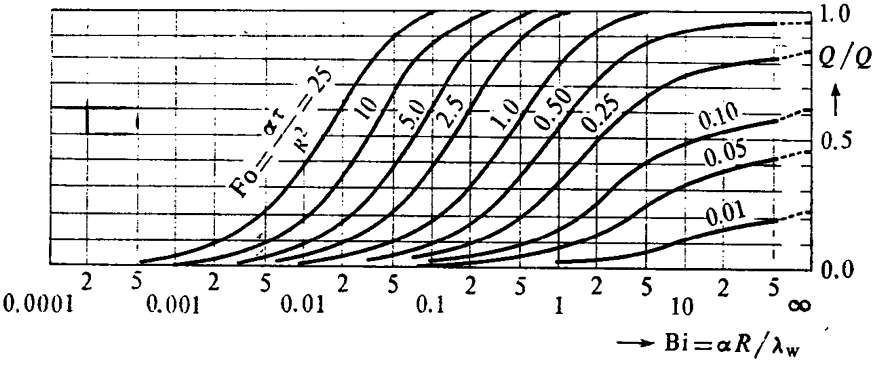


FIG. 25-4

25-3. Infinite Cylinder

Let us consider the cooling of a uniformly heated infinitely long cylinder of radius r situated in a medium at a lower constant temperature. The local coefficient of heat transfer from the surface of the cylinder to the surrounding medium does not change with time. The physical quantities c, ϱ and λ of the material are independent of temperature and are assumed to be known. It is necessary to determine the surface temperature, the temperature at the cylinder axis and the quantity of heat transferred from the cylinder to the surrounding medium for given moment of time.

When dealing with an infinitely long cylinder it is more expedient to relate the differential equation of conduction to cylindrical coordinates, with it being assumed that at the initial moment of time ($\tau=0$) the temperature over the cylinder volume is constant. Then

$$\frac{\partial\vartheta}{\partial\tau}=a\left(\frac{\partial^2\vartheta}{\partial r^2}+\frac{1}{r}\frac{\partial\vartheta}{\partial r}\right). \tag{25-9}$$

The cooling process for a cylinder is similar to that of a plate. Hence, the surface temperatures, the temperature at the cylinder axis in arbitrary time intervals are determined from the following relationships:

$$\frac{\vartheta_w}{\vartheta_1}=f(\mathrm{Bi},\ \mathrm{Fo});\quad \frac{\vartheta_{av}}{\vartheta_1}=f_1(\mathrm{Bi},\ \mathrm{Fo});$$

$$\frac{Q_\tau}{Q_0}=f_2(\mathrm{Bi},\ \mathrm{Fo}). \tag{25-10}$$

For the cylindrical wall

$$\mathrm{Bi}=\frac{\alpha r}{\lambda_w};\quad \mathrm{Fo}=\frac{a\tau}{r^2},$$

where r is the radius of the cylinder.

The quantities $\frac{\vartheta_w}{\vartheta_1}$, $\frac{\vartheta_{av}}{\vartheta_1}$ and $\frac{Q_\tau}{Q_0}$ are determined from the charts shown in Figs. 25-5, 25-6 and 25-7, and then it is easy to determine t_w, t_{av} and Q_τ from them.

The internal energy of a section of length l of the cylinder considered, measured from its value at the temperature of the surrounding medium which is taken to be zero, is found by formula

$$Q_0=\pi r^2 l\varrho c\vartheta_1. \tag{25-11}$$

25-4. The Sphere

Let us consider the cooling of a sphere with radius r whose mass has been heated uniformly to a constant temperature in a surrounding medium at a lower constant temperature. The physical constants c, ϱ and λ, and also the local heat-transfer coefficient are known. We wish to determine for any moment of time: the surface temperature, the temperature at the centre

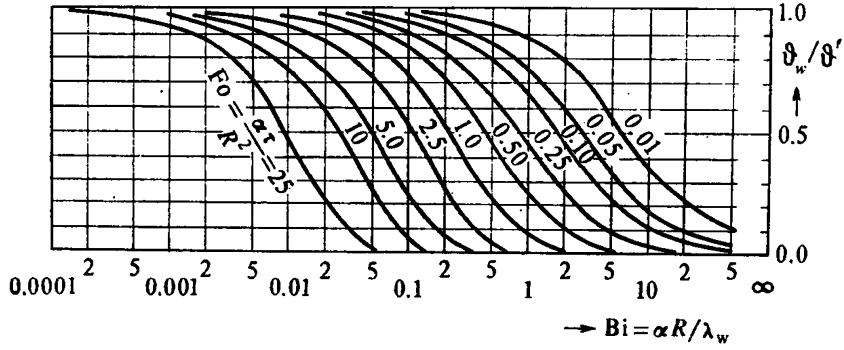


FIG. 25-5

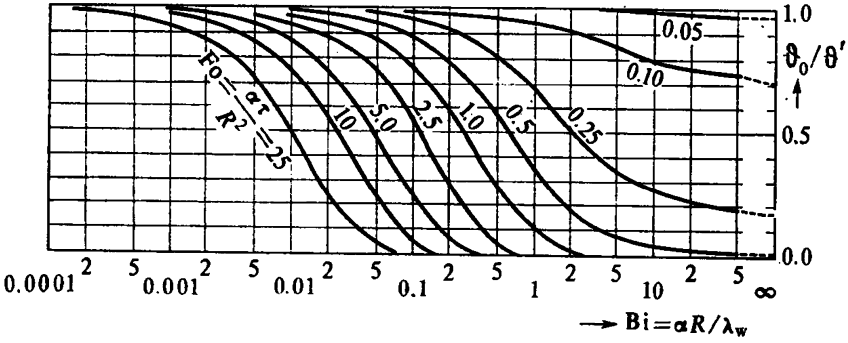


FIG. 25-6

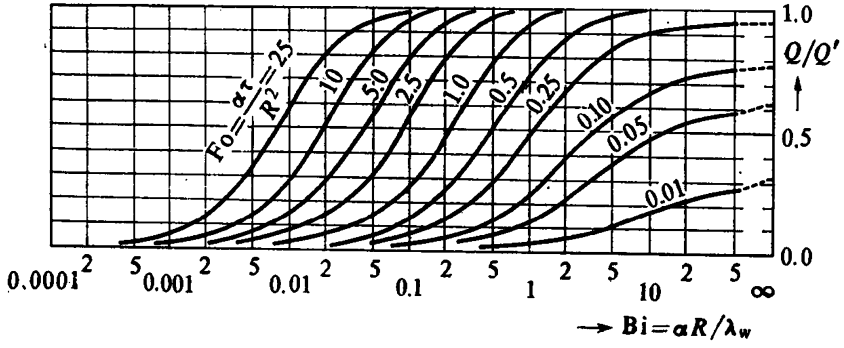


FIG. 25-7

of the sphere and the quantity of heat transferred from the sphere to the surrounding medium.

It is more convenient to reduce the differential equation of conduction to spherical coordinates

$$\frac{\partial \vartheta}{\partial \tau}=a\left(\frac{\partial^2 \vartheta}{\partial r^2}+\frac{2}{r}\frac{\partial \vartheta}{\partial r}\right). \tag{25-12}$$

The problem of the cooling of a sphere is similar to that of the cooling of a plate or cylinder [4]; the dimensionless terms $\frac{\vartheta_w}{\vartheta_1}$, $\frac{\vartheta_{av}}{\vartheta_1}$ and $\frac{Q_\tau}{Q_0}$ are functions of only two dimensionless numbers, Bi and Fo, and are determined from the relationships

$$\frac{\vartheta_w}{\vartheta_1}=f(\mathrm{Bi}, \mathrm{Fo}); \quad \frac{\vartheta_{av}}{\vartheta_1}=f(\mathrm{Bi}, \mathrm{Fo});$$

$$\frac{Q_\tau}{Q_0}=f(\mathrm{Bi}, \mathrm{Fo}).$$

For a sphere

$$\mathrm{Bi}=\frac{\alpha r}{\lambda_w}, \quad \mathrm{Fo}=\frac{a\tau}{r^2},$$

where r is the radius of the sphere.

Calculations for the cooling and heating of bodies can be found in [4].

The relationships between the dimensionless terms are found from the charts shown in Figs. 25-8, 25-9 and 25-10. Then the charts enable the determination of t_w, t_{av} and Q_τ.

The initial internal energy of the sphere is measured from its value at the temperature of the surrounding medium by formula

$$Q_0=\frac{4}{3}\pi r^3 \varrho c(t_0-t_m). \tag{25-13}$$

Example 25-1. Since the problems in cooling (heating) of an infinite plate, cylinder and sphere are solved in a similar way, it is sufficient to explain how to use the charts by considering only one example, the cooling of a cylinder.

Determine the surface temperature and the temperature at the axis of a very long steel cylinder with diameter 400 mm, which has been uniformly heated to 927 °C, one hour after it is placed in air whose temperature is 27 °C. The coefficient of heat transfer from the cylinder wall to the surrounding air $\alpha=50$ W/m^2·deg, the thermal conductivity of steel $\lambda=50$ W/m·deg, the heat capacity of steel $c=0.71$ kJ/kg·deg, the density of steel $\varrho=7900$ kg/m^3. Determine the temperatures after half an hour, with the same data.

Let us determine the temperature one hour after the cylinder is placed in the air.

The thermal diffusivity

$$a=\frac{\lambda_w}{c\varrho}=\frac{50}{710\times 7900}=8.9\times 10^{-6}\ \mathrm{m^2/s}.$$

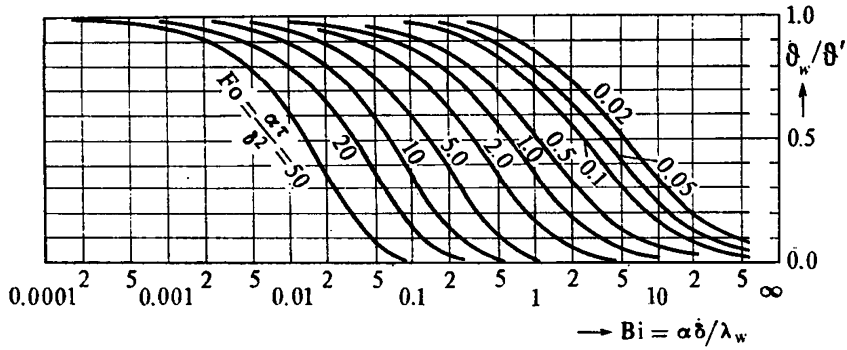


FIG. 25-8

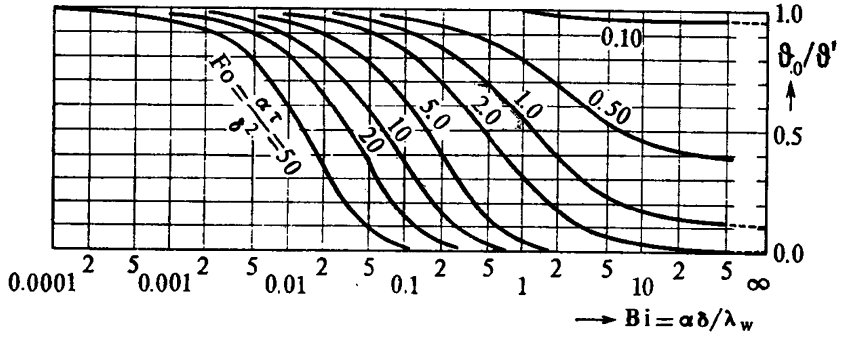


FIG. 25-9

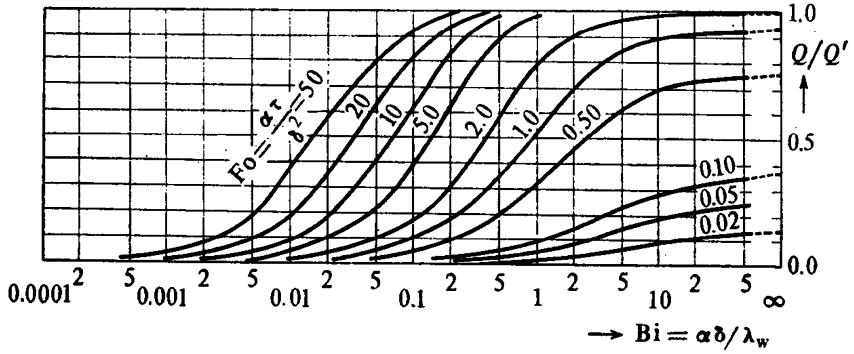


FIG. 25-10

The Biot (Bi) number

$$\mathrm{Bi}=\frac{\alpha r}{\lambda_w}=\frac{50\times 0.2}{50}=0.2.$$

The Fourier number

$$\mathrm{Fo}=\frac{a\tau}{r^2}=\frac{8.9\times 10^{-6}\times 3600}{0.04}=0.8.$$

Using the values of Bi and Fo, we find the dimensionless temperatures from the charts shown in Figs. 25-5 and 25-6

$$\frac{\vartheta_w}{\vartheta_1}=0.74; \quad \frac{\vartheta_{av}}{\vartheta_1}=0.80.$$

The temperature difference

$$\vartheta=t_0-t_m=927-27=900 \text{ °C}.$$

The surface temperature and the temperature at the cylinder axis after one hour are

$$\vartheta_w=0.74\times 900=666 \text{ °C} \quad \text{or} \quad t_w=\vartheta_w+t_w=666+27=693 \text{ °C};$$

$$\vartheta_{av}=0.8\times 900=720 \text{ °C} \quad \text{or} \quad t_{av}=\vartheta_{av}+t_m=720+27=747 \text{ °C}.$$

The loss of heat from the cylinder per hour is

$$\frac{Q_\tau}{Q_0}=f(\mathrm{Bi}, \mathrm{Fo}).$$

From the charts in Fig. 25-7 we find that $\frac{Q_\tau}{Q_0}=0.23$, i.e. in one hour the cylinder lost 23 per cent of its initial internal energy.

Let us now determine t_w and t_{av} and $\frac{Q_\tau}{Q_0}$ after 0.5 h.

The Biot and Fourier numbers

$$\mathrm{Bi}=0.2, \ \mathrm{Fo}=\frac{8.9\times 10^{-6}\times 1800}{0.04}=0.4$$

Then from the charts we find

$$\frac{\vartheta_w}{\vartheta_1}=0.85; \quad \frac{\vartheta_{av}}{\vartheta_1}=0.91.$$

The temperature difference

$$\vartheta_1=t_0-t_m=927-27=900 \text{ °C}.$$

The surface temperature

$$\vartheta_w=0.85\times 900=765 \text{ °C} \quad \text{or} \quad t_w=\vartheta_w+t_m=765+27=792 \text{ °C}.$$

The temperature at the cylinder axis

$$\vartheta_{av}=0.91\times 900=819 \text{ °C} \quad \text{or} \quad t_{av}=\vartheta_{av}+t_m=819+27=846 \text{ °C}.$$

The quantity of heat lost from the cylinder in 0.5 h is found from the charts to be $\frac{Q_\tau}{Q_0}=0.13$.

25-5. Regular-Regime Cooling (Heating) of Bodies

The cooling of a homogeneous isotropic body of arbitrary shape in a medium having constant temperature and a coefficient of heat transfer from the surface of the body, which is constant with respect to time, is determined by the differential equation of conduction

$$\frac{\partial t}{\partial \tau}=a\nabla^2 t \tag{25-14}$$

and the boundary conditions

$$\left(\frac{\partial t}{\partial n}\right)_{n=0}=-\left(\frac{\alpha}{\lambda}\right)(t_w-t_m),$$

$$(t)_{\tau=0}=f(x, y, z).$$

A solution of Eq. (25-14) at $t_m=\text{const}$ indicates that the variation of temperature at any point of the body follows an exponential law

$$\vartheta=\sum_{i=1}^{i=\infty} A_i U_i e^{-m_i \tau} \tag{25-15}$$

where $\vartheta = t_0-t_m$;

A_i = constants depending on the shape of the body and initial temperature distribution;

U_i = coordinates functions, which describe the temperature distribution in space;

m_i = a series of positive increasing constants ($m_1<m_2<m_3<\ldots<m_i$).

An analysis of Eq. (25-15) indicates that at small values of τ, from $\tau=0$ to $\tau=\tau_1$, the process of cooling (heating) depends on the initial conditions of cooling and is of a random nature, not associated with the conditions of cooling. This cooling stage is determined not only by the first, but also by the subsequent terms of the series (25-15). This cooling stage is referred to as the *first*, or *random, stage of cooling*.

With increasing time τ the series converges rapidly and all its terms, except the first one, tend to zero. With τ, exceeding some certain value, $\tau>\tau_1$, the initial conditions become of secondary importance and the process is fully determined only by the cooling conditions on the surface of the body, its physical properties and size (dimensions). The second cooling stage is called the stage of the *regular regime* of cooling and it is described by the first term of the series (25-15), i.e.

$$\vartheta=A_1 U_1 e^{-m_1 \tau} \tag{25-16}$$

Finding the logarithm of Eq. (25-16), we obtain

$$\ln \vartheta=\ln (AU)-m\tau=-m\tau+C(x, y, z). \tag{25-17}$$

It can be seen from Eq. (25-17) with the regular regime of conduction that the natural logarithm of the excess temperature ϑ at any point of the solid varies linearly with time.

Upon differentiation of the two sides of Eq. (25-17) with respect to time, we obtain

$$m=-\frac{1}{\vartheta}\frac{\partial\vartheta}{\partial\tau}, \quad \frac{1}{\mathrm{s}}. \tag{25-18}$$

The relative rate of temperature variation per unit time at any point of the body is independent of coordinates and time.

The quantity m is called the cooling *rate* of the regular regime. If we consider any point inside the body and measure its temperature, then the process of cooling can be represented by the curve $\vartheta=f(\tau)$ shown in Fig. (25-11). It is clear that the quantity m is equal to the slope of the curve

$$m=\frac{\ln\vartheta_1-\ln\vartheta_2}{\tau_2-\tau_1}. \tag{25-19}$$

The theory of regular-regime cooling (or heating) of bodies, developed by G. Kondratyev, is applicable to bodies of any shape. This theory relates the rate of regular-regime cooling, its physical and geometrical quantities and the external conditions of heat transfer. In the general case the quantity m is determined from equation

$$m=\psi F\frac{\alpha}{C}, \quad \frac{1}{\mathrm{s}}, \tag{25-20}$$

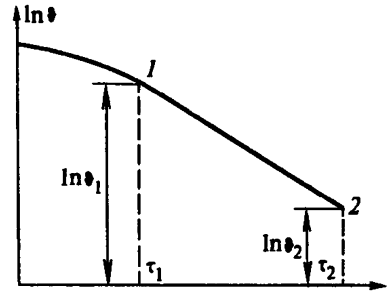


FIG. 25-11

i.e. the quantity m, characterizing the rate of cooling of a body, is directly proportional to the (local) heat-transfer coefficient α (if α does not tend to infinity), surface of the body F and inversely proportional to its total heat capacity $C=c\varrho V$; ψ is a dimensionless proportionality factor characterizing the non-uniform temperature distribution in the body and is a function of the Biot number.

Equation (25-20) expresses the energy conservation law for a body being cooled in a constant-temperature medium. If $\psi=1$, the temperature distribution in the body is uniform; when $\psi=0$, the temperature distribution becomes most non-uniform—the surface temperature is equal to that of the surrounding medium, and the temperature inside the body is not equal to the surface temperature.

If the heat-transfer coefficient $\alpha\to\infty$, then m is directly proportional to the thermal diffusivity of the cooled body

$$m_\infty=\frac{a}{K}, \quad \text{or} \quad a=Km_\infty, \tag{25-21}$$

where K is a proportionality factor depending on the size and shape of the body with dimension m^2. For instance, for a sphere

$$K=\left(\frac{r}{\pi}\right)^2,$$

and for a cylinder

$$K=\frac{1}{\left(\frac{2.405}{r}\right)^2+\frac{\pi}{l}},$$

where r = radius of cylinder;
l = length of cylinder.

On the basis of the theory of regular-regime cooling (heating) G. Kondratyev worked out methods of determining the thermophysical quantities a, λ and c for solids and fluids. These methods have found the widest application in engineering practice. The advantage of Kondratyev's method consists in the simplicity of experimental studies combined with the sufficient accuracy of test results.

Typical Questions to Chapter Twenty Five

1. What is a non-stationary temperature field?
2. Discuss the differential equation for transient conduction and its boundary conditions.
3. Discuss the equation of the temperature field for transient conduction.
4. What dimensionless terms are used to compose the equation of the temperature field?
5. Discuss the determination of the surface temperature of a plate, the temperature in the middle of the plate and of the quantity of heat transferred from the plate to the surrounding medium upon cooling.
6. Discuss the determination of the surface temperature, temperature at the axis of a cylinder and of the quantity of heat transferred from the cylinder to the surrounding medium upon cooling.
7. Discuss the determination of the surface temperature of a sphere, the temperature at the centre of the sphere and of the quantity of heat transferred from the cooled sphere to the surrounding medium upon cooling.
8. What differential equations describe the cooling of a homogeneous, isotropic and uniformly heated body of arbitrary shape, having a constant initial temperature?
9. What two periods, or stages, can be distinguished in the process of cooling a body with a constant initial temperature?
10. What is meant by the rate of regular-regime cooling and on what quantities does it depend?
11. What is meant by the proportionality factors for a sphere and cylinder?

CHAPTER TWENTY SIX

HEAT TRANSFER BY CONVECTION

26-1. Fundamentals of Heat Transfer by Convection

The second mode of heat transfer whereby heat is transported due to the motion of volumes of the medium in space takes place only in fluids (gases and liquids). Heat transfer by convection is always associated with conduction. The combined mode of simultaneous heat transfer by convection and conduction is referred to as *convective heat transfer.*

Two kinds of convection may be distinguished: *forced convection* (where motion is imparted to the fluid artificially) and *natural* (free) *convection* where motion of the medium arises because of heating and change of density.

In 1884, O. Reynolds proved experimentally that a moving fluid can flow in two ways or patterns, which obey different laws. When a fluid flows in the first way all particles of the fluid move only along directions that are parallel with one another and their motion coincides continuously with the direction of the entire stream. The fluid is in quiet motion, without pulsation, forming streams taking the shape of the conduit or passage. Flow of this type is referred to as *laminar.*

The second type of flow is called *turbulent* flow, and is characterized by continuous mixing of all layers of the fluid in flow. Each particle of the flow, moving along the conduit with some velocity, performs various motions in a direction perpendicular to the walls of the passage. In connection with this the flow is a random mass of irregularly moving particles. The more there is pulsing and vortexing, the greater the turbulence of flow. When there is a change from the laminar pattern of flow into the turbulent, the resistance due to friction in the conduit increases.

The pattern of fluid flow in a round tube was shown by O. Reynolds to be determined by the magnitude of the ratio $\frac{wd}{\nu}$ referred to as the *Reynolds number* and denoted by Re

$$\mathrm{Re}=\frac{wd}{\nu}, \tag{26-1}$$

where w = average fluid velocity, m/s;
d = diameter of round tube, m;
ν = kinematic viscosity of fluid, m^2/s.

For conduits, or ducts, of arbitrary cross section the concept of the

equivalent diameter is introduced, d_{eq}, which is substituted into the expression of the dimensionless term (see Sec. 27-1).

Substituting the dimensions of individual quantities into the Reynolds number, it can easily be seen that Re is dimensionless.

Up to Re=2000 the pattern of fluid flow in a tube remains laminar, at greater values of Re the pattern of flow changes from laminar to turbulent. Laminar flow is stable only in the subcritical region (up to Re=2000). When certain precautionary measures are undertaken laminar flow can be observed at Reynolds numbers considerably exceeding the critical number. However flow is unstable and the slightest disturbance causes a change from laminar flow to the turbulent flow.

The pattern of fluid flow influences the intensity, or rate, of heat transfer. With the laminar pattern of flow in the absence of natural convection, heat is transferred in the direction perpendicular to the wall only by conduction. The quantity of heat transferred depends on the physical properties of the fluid (liquid or gas), dimensions, and the geometrical shape of the surface of the conduit, and is almost independent of fluid flow velocity.

With fluid in turbulent flow, heat is transported by particles moving in a direction perpendicular to the surface of the conduit as well as by conduction.

Physical Properties of Fluids

In engineering, air, water, gases, oil, petroleum, alcohol, mercury, molten metals and many other substances are used as liquid or gaseous heat-carrying agents. Depending on the physical properties of these substances, the processes of heat transfer proceed in different ways.

Heat transfer is greatly influenced by the following physical parameters: thermal conductivity λ, specific heat capacity c, density ϱ, thermal diffusivity a and the coefficient of dynamic viscosity μ. These parameters have a certain value for each substance, and are a function of temperature and in some cases also of pressure.

The quantities λ, c, a and ϱ were already considered in the preceding sections. In studying heat transfer by convection viscosity is also very important. All real liquids are viscous; there is always internal friction (a tangential force) between particles or layers moving at different velocities. It accelerates the motion of layers flowing at lower velocities and decelerates the motion of layers moving at higher velocities. In accordance with Newton's law the magnitude of the frictional forces between layers of unit area is proportional to the velocity gradient dw/dn along the normal to the direction of fluid flow. Hence,

$$S=\mu\frac{dw}{dn},$$

where μ is the proportionality factor depending on the nature of the fluid

and its temperature and referred to as *dynamic viscosity* or the *internal friction coefficient*, N·s/m².

As μ increases the fluidity of a liquid decreases. The viscosity of liquids diminishes with rising temperature and is almost independent of pressure. The viscosity of gases increases with increasing temperature and pressure. The viscosity of ideal gases is independent of pressure.

In addition to dynamic viscosity, equations describing hydrodynamic and heat-transfer phenomena sometimes include the kinematic viscosity coefficient ν, which is the ratio of the dynamic viscosity to the fluid density $\nu = \mu/\varrho$ m²/s.

The coefficients μ and ν are physical parameters determined by experiment.

Patterns of Flow and the Boundary Layer

Theoretical studies of convective heat transfer are based on the theory of the boundary layer suggested by L. Prandtl in 1904.

Let us consider some body exposed to an infinite longitudinal flow of fluid. Fluid velocity w is constant (Fig. 26-1). Due to the influence of frictional forces in the immediate vicinity of the surface of the body, the

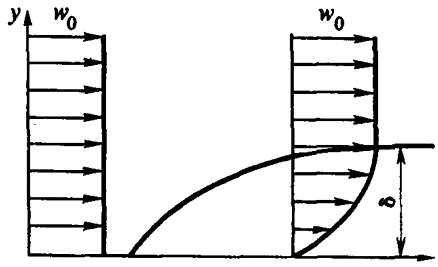


FIG. 26-1

velocity of flow must rapidly drop to zero. The thin layer of fluid close to the surface of the body, where the fluid velocity changes from the free-stream flow velocity away from the wall to zero right at the wall, is called the *dynamic boundary layer* (Fig. 26-1). The thickness of this layer, δ, increases along the direction of flow.

With an increase in the velocity of fluid flow, the thickness of the dynamic boundary layer decreases due to its being carried off by the fluid flow. On the other hand, an increase of viscosity causes an increase of the thickness of the dynamic boundary layer.

In the dynamic boundary layer the fluid can be in both turbulent *1*, and laminar *2* patterns of flow (Fig. 26-2). The pattern of flow and the thickness of the boundary layers (δ_l or δ_t) are mainly determined by the magnitude of the Reynolds number.

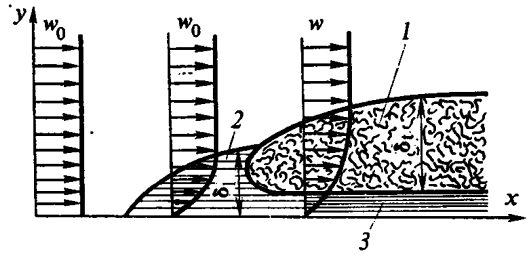


FIG. 26-2

It will be noted that in the event of a turbulent dynamic boundary layer there is a very thin layer of liquid in laminar flow right at the wall, which is referred to as the *viscous*, or *laminar*, *sublayer 3*.

If the wall and fluid are at different temperatures, then a *thermal boundary layer* forms near the wall, in which all variation of fluid temperature takes place (Fig. 26-3). Outside the boundary layer fluid temperature is constant

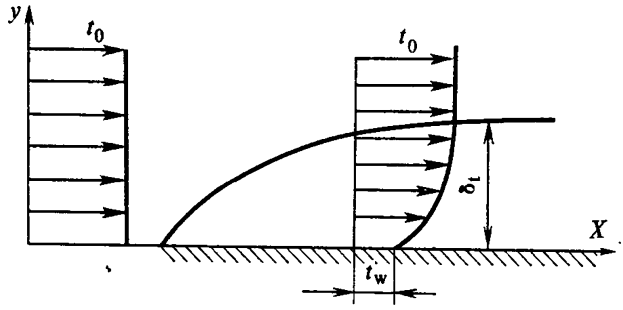


FIG. 26-3

and denoted by t_0. In general the thicknesses of the thermal and dynamic boundary layers do not coincide (Fig. 26-4). The relation between the thicknesses of the dynamic and thermal boundary layers is determined by the magnitude of the dimensionless term, the Prandtl number, $Pr=\nu/a$. For viscous liquids with a low thermal conductivity (oils, for instance) $Pr>1$ and the dynamic boundary layer is thicker than the thermal boundary layer. For gases $Pr\approx 1$ and the layers are approximately of the same thickness. For liquid metals $Pr<1$ and the thermal boundary layer penetrates in the region of the dynamic undisturbed.

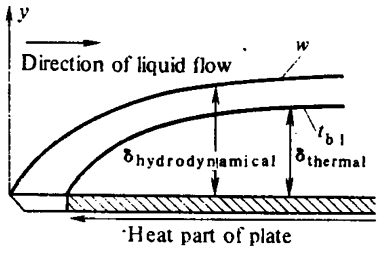


FIG. 26-4

The mechanism and intensity of heat transfer depend on the pattern of fluid flow in the boundary layer. If the fluid is in laminar flow in the boundary layer,

then, in the direction perpendicular to the wall, heat is transferred by conduction. However at the external border of the layer, where temperature varies only slightly in the direction perpendicular to the wall, heat transfer by convection prevails along the wall.

With turbulent fluid flow in the thermal boundary layer heat transfer in the direction perpendicular to the wall is mainly due to turbulent mixing of the fluid. This kind of heat transport proceeds at a rate much greater than the rate of heat transfer by conduction. However, right at the wall, in the laminar sublayer, heat is transferred to the wall by ordinary conduction.

The change of physical properties of fluid in the boundary layer depends on the temperature, and the intensity of heat transfer between the fluid and wall proves to be different, depending on whether the fluid is being heated or cooled. With liquids, for instance, the intensity of heat transfer upon heating is greater than upon cooling, due to the decrease of the thickness of the boundary layer. Consequently, the intensity of heat transfer depends on the direction of the flow of heat.

With convective heat transfer, the shapes and sizes of surfaces are very important; they may change the character of fluid flow and the thickness of the boundary layer sharply.

26-2. Heat-Transfer Coefficient. Differential Equation of Heat Transfer

Heat transfer by convection depends greatly on the character of the fluid flow, since it determines the mechanism of this mode of heat transfer. The process of heat transfer at the interface between the wall of a channel and the boundary layer can be expressed by Fourier law

$$dQ = -\lambda\, dF \left(\frac{\partial t}{\partial n}\right)_{n=0}, \tag{26-2}$$

where n is the normal to the surface of the body (wall).

The same quantity of heat may be expressed by Newton's law

$$dQ = \alpha\, dF(t_f - t_w). \tag{26-3}$$

Combining the two equations, we obtain:

$$-\lambda \left(\frac{\partial t}{\partial n}\right)_{n=0} = \alpha\, \Delta t, \quad \text{or} \quad \alpha = -\left(\frac{\lambda}{\Delta t}\right)\left(\frac{\partial t}{\partial n}\right)_{n=0}. \tag{26-4}$$

The differential equation of heat transfer (26-4) describes the process of heat transfer on the surface of a channel ($n=0$).

By its physical nature, convective heat exhange is a rather intricate process and depends on a great number of factors determining the process of local heat transfer. The coefficient of heat transfer characterizes the rate of heat exchange between the liquid and conduit surface. In the general case the (local) heat-transfer coefficient is a function of the physical parameters

of the fluid involved, the pattern of fluid flow, the fluid flow velocity, the shape and size of the body and other factors.

Hence, the heat-transfer coefficient

$$\alpha=f(w, \lambda, \mu, \varrho, c, X, t_f, t_w, \Delta t, \Phi, l_1, l_2, l_3, \ldots), \tag{26-5}$$

where X = the pattern of fluid flow (natural or forced convection);
Φ = shape of the wall;
l_1, l_2, l_3 = dimensions of the surface.

Equation (26-5) indicates that the heat-transfer coefficient is a complicated quantity and no general determination formula can be devised for it. The quantity α is usually determined experimentally.

Applying general laws of physics, it is possible to form differential equations of convective heat exchange for a given process, taking into account both thermal and dynamic phenomena.

The system of differential equations consists of the equations of energy (or heat conduction), local heat transfer, flow and continuity.

The differential equation of energy establishes the connection between space and time changes in temperature at any point of a fluid in flow

$$\frac{\partial t}{\partial \tau}+w_x\frac{\partial t}{\partial x}+w_y\frac{\partial t}{\partial y}+w_z\frac{\partial t}{\partial z}=\frac{\lambda}{c_p\varrho}\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right)=a\,\nabla^2 t. \tag{26-6}$$

When $w_x=w_y=w_z=0$, the equation of energy reduces into the equation of conduction for solids (if there are no inner heat sources).

The differential equation of heat transfer expresses the conditions of heat transfer on the boundary between a solid and a fluid

$$\alpha=-\left(\frac{\lambda}{\Delta t}\right)\left(\frac{\partial t}{\partial n}\right)_{n=0}. \tag{26-7}$$

The differential equation of flow for a viscous incompressible fluid (liquid) is represented by the Navier-Stokes equation

for the x-axis

$$\varrho\left(\frac{\partial w_x}{\partial \tau}+\frac{\partial w_x}{\partial x}w_x+\frac{\partial w_x}{\partial y}w_y+\frac{\partial w_x}{\partial z}w_z\right)=\varrho g_x-\frac{\partial p}{\partial x}+\mu\left(\frac{\partial^2 w_x}{\partial x^2}+\frac{\partial^2 w_x}{\partial y^2}+\frac{\partial^2 w_x}{\partial z^2}\right);$$

for the y-axis

$$\varrho\left(\frac{\partial w_y}{\partial \tau}+\frac{\partial w_y}{\partial x}w_x+\frac{\partial w_y}{\partial y}w_y+\frac{\partial w_y}{\partial z}w_z\right)=\varrho g_y-\frac{\partial p}{\partial y}+\mu\left(\frac{\partial^2 w_y}{\partial x^2}+\frac{\partial^2 w_y}{\partial y^2}+\frac{\partial^2 w_y}{\partial z^2}\right); \tag{26-8}$$

for the z-axis

$$\varrho\left(\frac{\partial w_z}{\partial \tau}+\frac{\partial w_z}{\partial x}w_x+\frac{\partial w_z}{\partial y}w_y+\frac{\partial w_z}{\partial z}w_z\right)=\varrho g_z-\frac{\partial p}{\partial z}+\mu\left(\frac{\partial^2 w_z}{\partial x^2}+\frac{\partial^2 w_z}{\partial y^2}+\frac{\partial^2 w_z}{\partial z^2}\right).$$

This equation is valid both for the laminar and turbulent patterns of flow. In the event of turbulent flow w represents the real (instantaneous) velocity, equal to the sum of the average and fluctuating velocities.

For compressible fluids the *differential equation of continuity* has the following appearance:

$$\frac{\partial \varrho}{\partial \tau}+\frac{\partial(\varrho w_x)}{\partial x}+\frac{\partial(\varrho w_y)}{\partial y}+\frac{\partial(\varrho w_z)}{\partial z}=0. \tag{26-9}$$

For incompressible fluids at $\varrho=\text{const}$ the equation of continuity takes the following form

$$\frac{\partial w_x}{\partial x}+\frac{\partial w_y}{\partial y}+\frac{\partial w_z}{\partial z}=0. \tag{26-10}$$

The derivation of differential equations, (26-6)-(26-10), involves cumbersome mathematical computations which can be found in special courses in fluid mechanics and heat transfer.

26-3. Theoretical Fundamentals of Similarity

In the study of various physical phenomena two methods of investigation are used to obtain quantitative laws. The first method is the experimental investigation of the properties of a particular phenomenon, while the second method is the theoretical investigation of a problem.

The advantage of the experimental method of investigation is the reliability of the results obtained. Also, when conducting an experiment it is possible to concentrate on studying the quantities that are of the great practical interest.

The main drawback of the experimental method of investigation is that the results of a given experiment cannot be applied directly to another phenomenon which differs in some respects from that under investigation. Hence the conclusions based on the analysis of a given experimental investigation cannot be applied to other phenomena. So, when using the experimental method of investigation each particular case must be studied individually. This is an inherent shortcoming of the experimental method.

The second research method, used to find quantitative relationships, is exemplified by mathematical or theoretical physics, and is widely used in contemporary science.

In deriving the differential equations of theoretical physics, use is made of the general laws of nature which in turn are the result of very wide generalizations of experimental results. The application of these general laws to phenomena under investigation makes it possible to find connections between the physical parameters of a phenomenon.

As a good example we may consider the derivation of the Fourier differential equation of conduction in the course of which the specific circumstances of the phenomenon were ignored and only a differential volume of the solid, dV, was considered. The derivation of the equation was based on a single experimental fact according to which redistribution of energy in a medium is possible only when the temperature gradients are not equal to zero. Hence the derived equation relates in the most general way the quanti-

ties essential for the phenomenon, and characterizes their inherent properties in all phenomena of the given class (class of heat conduction phenomena). The differential equation contains no data on the actual magnitudes of individual quantities describing a phenomenon. The variables in the equation may take different values yet each be in accord with some phenomenon.

Thus, any differential equation (or system of equations) is the mathematical model of a whole class of phenomena. It follows that by the term *class is meant such a totality of phenomena characterized by the same processes and an identical physical nature.*

The phenomena of such a class obey the same equations both in their appearance and in the physical meaning of their component terms. For instance, the differential equation of conduction

$$\frac{\partial t}{\partial \tau}=a\left(\frac{\partial^2 t}{\partial x^2}\right)$$

describes a whole class of phenomena of transient conduction having a common process.

The differential equation describing transient transport of substance (Fourier law) can also be presented in the form

$$\frac{\partial C}{\partial \tau}=D\left(\frac{\partial^2 C}{\partial x^2}\right), \tag{26-11}$$

where D = coefficient of diffusion;
C = concentration of some substance.

Equation (26-11) is similar in form to the differential equation of conduction, but it describes another class of phenomena, since its component terms have another physical meaning.

By integrating a differential equation, we can obtain an infinite number of different solutions satisfying the equation.

In order to choose from the multitude of solutions one particular solution, it is necessary to know all the specific features of the given phenomena which differentiate it from the whole class of homogeneous phenomena. These supplementary conditions which together with the differential equation uniquely determine a single phenomenon are referred to as the *conditions of single-valuedness or conditions of unambiguity*. These conditions must contain all the peculiar features of the given particular phenomenon.

The conditions of unambiguity are characterized by the following individual features, singling them out from a whole class of phenomena. They consist of the following: (1) geometrical conditions characterizing the shape and size of a body or system; (2) physical conditions defining the physical properties of the bodies composing the given system; (3) boundary conditions characterizing the interaction of the system with the surrounding medium, i.e. characterizing the peculiarities of the process taking place at he boundaries of bodies; (4) time conditions characterizing the development

of a process at the initial moment of time over the entire volume of a system (for steady-state processes no time conditions are needed).

The differential equations and the four conditions of unambiguity define a particular single phenomenon. In most cases and, in particular, when describing convective heat transfer, owing to the complexity and intricacy of the phenomena studied, it is impossible to find a solution satisfying the differential equation and the conditions of unambiguity.

Consequently, while the drawback of the experimental method of investigation is that it is impossible to apply the results of an experimental study to other phenomena, differing from the investigated one, the drawback of mathematical physics is that it is in general impossible to pass from the class of phenomena characterized by differential equations and conditions of unambiguity to the particular phenomenon. Individually, each of these methods cannot be used effectively to solve practical problems.

By combining the positive merits of the mathematical and experimental methods of investigating physical phenomena, it is possible to obtain a universal method for studying various natural phenomena. Such a combination of the two methods is provided by the *theory of similarity*.

The theory of similarity makes it possible to draw a number of conclusions from the differential equations and conditions of unambiguity without resorting to integration and provides a theoretical basis for conducting experiments and for the treatment and generalization of test data.

Apart from using the concepts of a class of an individual phenomenon, the theory of similarity makes use of the concept of a group of phenomena. The name *group of phenomena* is given to a totality of physical processes described by differential equations of the same form and by dimensional conditions of unambiguity of the same form. Individual physical processes belonging to a given group of phenomena only differ in the numerical magnitudes of the quantities present in the dimensional conditions of unambiguity. A group of phenomena unites all the processes to which the results of a single experiment can be applied. The concept of the group of phenomena is not as comprehensive as that of the class of phenomena, but it is wider than the concept of a single phenomenon.

In the theory of similarity a group of phenomena is obtained by multiplying each of the component quantities of the conditions of unambiguity by constant numerical factors. These multipliers may be different for various physical quantities.

The method of constructing a group of phenomena can be elucidated by considering geometrical figures by way of example. Shown in Fig. 26-5 are various rectangles. The concept of a "rectangle" defines a whole class of plane figures all of which have the common property of having four angles all equal to right angles. To select from a whole class of figures (Fig. 26-5*a*) a single figure, it is necessary to know the numerical values of sides l_1 and l_2 that serve as conditions of unambiguity. A group of similar figures (Fig. 26-5*b*) can be obtained by multiplying the sides of the main figure by the quantity K_l which can be assigned any arbitrary values.

In doing so, we can obtain a whole number of figures similar to one another, since their sides are proportional:

$$\frac{l_1''}{l_1'}=\frac{l_2''}{l_2'}=K_l.$$

The quantities K_l are *transformation factors* or *similarity constants*. When a group of figures is constructed in this way each rectangle differs from another within the given group only in its scale. For each point of one

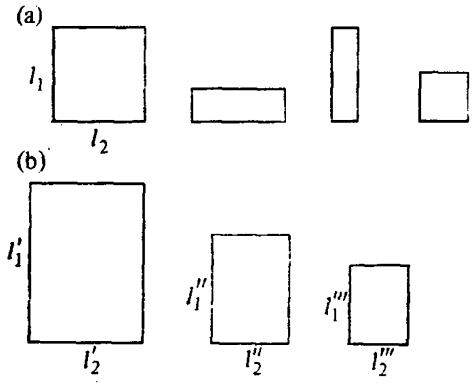


FIG. 26-5

figure there is a corresponding point on the other figure. Transformations of this kind are called *similar*. The principles of similarity are applicable not only to geometrical bodies, but also to physical and thermal processes.

Dimensionless Terms (Criteria of Similarity)

The similarity constants are the same for finite and infinitesimal quantities.

Let the lengths of two sections of a straight line, l' and l'', be related by a constant of geometrical similarity C_l. Should we take parts of these sections l_1' and l_1'', corresponding to constant C_l, then

$$\frac{l''}{l'}=\frac{l_1''}{l_1'}=C_l=\frac{l''-l_1''}{l'-l_1'}=\frac{\Delta l''}{\Delta l'}.$$

Upon passing to the limit we obtain

$$C_l=\frac{dl''}{dl'}.$$

It follows that the similarity constant gives the relationship between not only the corresponding parameters, but also the finite and infinitesimal increments of these parameters.

Let us consider the rule governing the choice of the similarity constants by treating a particular example, using for this purpose of the differential

equation of heat transfer (26-4). For corresponding points of two similar systems this equation takes the following form:

for the first system

$$\alpha' = -\left(\frac{\lambda'}{\Delta t'}\right)\left(\frac{\partial t'}{\partial n'}\right), \tag{a}$$

for the second system

$$\alpha'' = -\left(\frac{\lambda''}{\Delta t''}\right)\left(\frac{\partial t''}{\partial n''}\right). \tag{b}$$

Let us denote the similarity constants:

$$C_\alpha = \frac{\alpha''}{\alpha'}; \quad C_\lambda = \frac{\lambda''}{\lambda'};$$

$$C_t = \frac{\Delta t''}{\Delta t'}; \quad C_l = \frac{n''}{n'} = \frac{l''}{l'}, \tag{c}$$

where l is the reference dimension of the system.

It follows from the definition of the similarity constants that

$$\alpha'' = C_\alpha \alpha'; \quad \lambda'' = C_\lambda \lambda'; \quad \Delta t'' = C_t \Delta t';$$
$$t'' = C_t t'; \quad n'' = C_l n'.$$

Substituting these expressions into Eq. (b) and cancelling C_t, we obtain

$$\alpha' = \frac{C_\lambda}{C_\lambda C_l} \frac{\lambda'}{\Delta t'} \frac{\partial t'}{\partial n'}. \tag{d}$$

Equations (a) and (d) are identical since they express the relation between the parameters of a process stemming from the differential equation of heat transfer for the same point of a system. It follows from the conditions of identity of equations that

$$\frac{C_\lambda}{C_\lambda C_l} = 1 = C. \tag{e}$$

This expresses the relation between similarity constants obtained from the differential equation (26-4).

It can be seen from Eq. (e) that the choice of a set of similarity constants is limited by the condition that the above combination of similarity constants in any case must be equal to unity. The quantity C is referred to as the *similarity indicator*.

Replacing the similarity constants in Eq. (e) by these taken from Eq. (c), we obtain

$$\frac{\alpha' l'}{\lambda'} = \frac{\alpha'' l''}{\lambda''}. \tag{f}$$

It follows that there exist dimensionless ratios of parameters characterizing a process that have the same numerical values at corresponding points.

These dimensionless ratios are called *dimensionless terms* or *criteria of similarity.*

It is generally accepted to give the dimensionless terms the names of scientists famous for their work in the field of heat transfer and fluid dynamics. The dimensionless term expressed by Eq. (f) is called the *Nusselt number* and is denoted by Nu.

Equality (f) can be presented in the form

$$\mathrm{Nu}=\frac{\alpha l}{\lambda}=\text{idem.}$$

Any ratio of any two homogeneous quantities is called a *simplex.* By *homogeneous* are meant physical quantities having the same physical meaning and dimensionality.

The products of numbers and their quotients after division are also dimensionless terms or criteria of similarity. Similarity of phenomena can be characterized by similarity constants and dimensionless terms. The similarity constants preserve their numerical values only for two similar phenomena; they remain the same for all the corresponding points of all similar systems considered, but their numerical values may differ at different points of one system.

The criteria of similarity are new variables whose introduction reduces considerably the number of arguments of a function. The quantitative relation between dimensionless terms is established experimentally.

The direction in which an experiment is to be conducted is indicated by dimensional analysis and the theory of similarity.

The two theories make it possible to find the unknown connections between physical parameters of phenomena being investigated in the form of relationships between the dimensionless complexes composed of these physical parameters. However, the initial prerequisites and the methods of composing dimensionless complexes differ.

Dimensional analysis is used when the relating equations are not known or when a new complex process is considered for which no analytical description yet exists. There should then be available a complete list of quantities essential for the investigated phenomenon and it is not necessary to work out differential equations and conditions of unambiguity. Such a list of dimensional quantities can be used to find dimensionless groups and to work out criterion equations. All this constitutes the great importance of dimensional analysis. The weakness of dimensional analysis is that it is possible to obtain inexact or even erroneous solutions, when all the quantities, characterizing the phenomenon are not considered and when the physical essence of the phenomenon is not clear.

The theory of similarity can be applied not only when the list of the quantities essential for the phenomenon under consideration is available, but also when there is a system of differential equations relating the physical quantities, associated with the phenomenon. These equations must be formulated for the special case being investigated. The addition of the

conditions of unambiguity to the equations makes the investigation specific and enables the theory of similarity to be used. In all cases when the differential equations relating physical quantities can be solved, the method employing analysis of the equations is the only correct way for applying the theory of similarity. Thus, the merit of the theory of similarity consists in the reliability of the solutions obtained with the aid of this theory. The solutions obtained are as reliable as those obtained purely analytically.

The two theories however require a thorough checking of the results obtained by conducting special experiments.

Theorems of Similarity (Similitude)

The theory of similarity, or similitude, of physical phenomena is based on three theorems. Two of them deal with phenomena whose similarity is known beforehand and they formulate the main properties of similar phenomena. The third theorem is a converse one. It establishes the criteria, making it possible to determine whether or not two phenomena are similar to each other.

The first theorem of similarity for similar flow of two fluids was first proposed by Newton in 1686; however a strict proof of the theorem was given by J. Bertrand in 1848.

In proving the theorem, Bertrand departed from the most common equation of mechanics, d'Alembert principle:

$$\Sigma\left[\left(X-m\frac{d^2X}{d\tau^2}\right)\delta X+\left(Y-m\frac{d^2Y}{d\tau^2}\right)\delta Y+\left(Z-m\frac{d^2Z}{d\tau^2}\right)\delta Z\right]=0,$$

where $X,\ Y,\ Z$ = the projections of forces acting upon a mass;
$\frac{d^2X}{d\tau^2},\ \frac{d^2Y}{d\tau^2},\ \frac{d^2Z}{d\tau^2}$, etc. = the projections of their accelerations.

However, we can use as an initial equation Newton's second law of motion instead of the formulae of analytical mechanics.

Let us suppose that there are two mechanical systems in similar motion. The two phenomena are described by the same equation

$$f'=m'\frac{dw'}{d\tau'} \tag{a}$$

$$f''=m''\frac{dw''}{d\tau''}. \tag{b}$$

The existence of similarity between the two phenomenon imposes the following conditions on them:

$$f''=C_f f'; \quad m''=C_m m'; \quad w''=C_w w''; \quad \tau''=C_\tau \tau'. \tag{c}$$

Substituting the expressions for the quantities of the second phenomenon in terms of the quantities of the first phenomenon from Eq. (a) into Eq. (b), we obtain

$$\left(\frac{C_f C_\tau}{C_m C_w}\right)f'=m'\frac{dw'}{d\tau'}. \tag{d}$$

Thus, there are two equations (a) and (d) which relate between them the like quantities f', m', w', τ'. These equations are identical, and it follows from the conditions of identity that

$$\frac{C_f C_\tau}{C_m C_w} = C = 1. \qquad \text{(e)}$$

The similarity indicator of similar phenomena is equal to unity.

Equation (e) is the mathematical expression of the first theorem of similarity, or similitude, stating that for *similar phenomena the similarity indicators are equal to unity.*

Substituting into Eq. (e) the values of the quantities from expression (c), we obtain

$$\frac{f'\tau'}{m'w'} = \frac{f''\tau''}{m''w''}.$$

This equality indicates that the similarity criterion $f\tau/mw$ is the same for all phenomena similar to each other.

The dimensional number obtained is named after Newton and denoted by the initial letters Ne.

It follows that the equality can be presented in the form

$$\mathrm{Ne} = \frac{f\tau}{mw} = \text{idem}.$$

The first theorem of similarity can also be formulated as follows: *for similar phenomena the criteria of similarity are numerically equal.*

Thus, the first theorem of similarity relates the similarity constants and makes it possible for them to compose the criteria of similarity, or dimensionless terms. The theorem indicates that when conducting an experiment it is necessary and sufficient to measure only the quantities present in the dimensionless terms for the phenomena investigated.

The second theorem of similarity was proved in 1911 by the Russian scientist A. Federman and in 1914 by the American scientist E. Buckingham.

From the foregoing the following conclusions may be drawn for it to be possible to compose dimensionless terms or criteria of similarity there must be available an analytical relationship between the physical quantities characterizing a given phenomenon (for instance, the equation of motion). If the equation is given in differential form, the determination of the criteria of similarity does not require its integration. For instance, the Nu and Ne numbers were obtained directly from the differential equations without integration. The possibility of obtaining dimensionless terms from differential equations is very important when the latter cannot be integrated.

The second theorem of similarity states that *if a physical phenomenon is described by a system of differential equations, it is always possible to represent them in the form of criterion equations,* i.e. *the integral of a differential equation* (or of a system of equations) *can be represented as a function of the dimensionless terms of the differential equation.*

The second theorem states that integration does not change the appearance of the dimensionless terms. For instance, the equation for the velocity of a fluid particle is $w=dl/d\tau$. The equation after integration, assuming that during the time interval τ the velocity remains unchanged, is $w=l/\tau$, which gives the same homochronicity number Ho:

$$\mathrm{Ho}=\frac{w\tau}{l}=\text{idem}.$$

It follows from the second theorem of similarity that if the results of any experiment are treated using dimensionless terms, the relationship between them must be expressed by a criterion equation. By a *criterion equation* is meant an equation which represents any relationship between quantities characterizing a given phenomenon as a relationship amongst dimensionless terms $K_1, K_2, K_3, \ldots, K_n$ i.e.

$$f(K_1, K_2, K_3, \ldots, K_n)=0.$$

The third theorem of similarity establishes the conditions required for two phenomena to be similar to each other. This theorem was formulated by M. V. Kirpichev and A. A. Gukhman, and proved by Kirpichev in 1933.

The third theorem stems from the assumption that phenomena proceed in geometrically similar systems (from this, geometrical similarity of systems is the first necessary condition for the existence of similarity), that it is possible to formulate differential equations for the phenomenon considered, that the existence and uniqueness of the solution of the equation under the given boundary conditions is established, and also that the numerical values of the coefficients and physical parameters present in the differential equation are known.

The enumerated conditions are called the *conditions of unambiguity (single-valuedness) of a phenomenon.* The conditions of unambiguity single out from the whole group of phenomena described by a differential equation, one unique particular phenomenon. So, the similarity of the conditions of unambiguity is the second necessary condition of similarity.

A supplementary condition of similarity is the equality of the dimensionless terms composed only from the quantities present in the conditions of unambiguity. Such dimensionless terms are referred to as the *reference terms.* If two phenomena have similar conditions of unambiguity, their dimensionless terms are the same. The dimensionless terms containing unknown quantities are referred to as *unknown terms.* The third theorem states that the addition of the third supplementary condition to the preceding conditions is sufficient for phenomena to be similar.

Thus, the third theorem of similarity can be stated in the following manner: *phenomena are similar whose conditions of unambiguity are similar and whose dimensionless terms, formed from the conditions of unambiguity, are numerically equal.*

If the conditions of unambiguity are similar and the reference dimensionless terms are numerically equal, then all other unknown dimensionless

terms are equal. It follows from this that *each of the unknown dimensionless terms is a single-valued function of the totality of reference dimensionless terms.* This conclusion is of great importance for the generalization of experimental results.

The theory of similarity provides a general systematic method to be followed in any particular case when analyzing equations describing a phenomenon. It establishes the correct way of setting up an experiment and treating the results obtained. Consequently, the conducting of an experiment and the treatment of the results of an experimental study of a complex process such as convective heat transfer may be put on a scientific basis, and the results gain significant theoretical and practical value. The theory of similarity also establishes the conditions in which the results of experimental investigations and studies can be applied to other phenomena similar to that investigated. But if a particular phenomena is considered which must be investigated on a scale model, then the theory of similarity provides methods to be followed for designing and building a model similar to full-scale size equipment or apparatus. In conclusion, we can say that the theory of similarity is the scientific foundation for conducting experimental studies of heat transfer and generalizing experimental results.

26-4. Reduction of Differential Equations of Convective Heat Transfer and of Conditions of Unambiguity to Dimensionless Form

For practical application of the theory of similarity to cases of convective heat transfer described by a system of differential equations and conditions of unambiguity with a large number of variables, it is first of all necessary to know the dimensionless terms which will be the component terms of the criterion equations.

A system of differential equations, such as the differential equations describing heat transfer between a solid and its surrounding medium, the equations of energy or conduction, in a moving fluid, the equation of viscous incompressible fluid flow (the Navier-Stokes equation) or the continuity equation, enables us to find out the structure of these dimensionless terms.

The indicated system of equations gives together with the conditions of unambiguity a complete mathematical description of heat transfer by convection, but an analytical solution of the system encounters great difficulties. The theory of similarity enables these difficulties to be overcome by combining dimensional physical quantities into dimensionless groups, or complexes, in such a way that the number of groups is less than the number of quantities making up these groups. This considerably simplifies the investigation of physical processes. The dimensionless groups so obtained can be considered as new variables.

Thus the dimensionless terms can be obtained by using the following equations:

The Navier-Stokes equation of flow for a viscous fluid is

$$\varrho\left(\frac{\partial w_x}{\partial \tau}+w_x\frac{\partial w_x}{\partial x}+w_y\frac{\partial w_x}{\partial y}+w_z\frac{\partial w_x}{\partial z}\right)=\varrho g_x-\frac{\partial p}{\partial x}+\mu\left(\frac{\partial^2 w_x}{\partial x^2}+\frac{\partial^2 w_x}{\partial y^2}+\frac{\partial^2 w_x}{\partial z^2}\right) \tag{26-12}$$

(in order to shorten the calculations the Navier-Stokes equation is given here only for the x-axis);

the continuity equation for an incompressible fluid

$$\frac{\partial w_x}{\partial x}+\frac{\partial w_y}{\partial y}+\frac{\partial w_z}{\partial z}=0; \tag{26-13}$$

the equation of energy for fluid in flow

$$\frac{\partial t}{\partial \tau}+w_x\frac{\partial t}{\partial x}+w_y\frac{\partial t}{\partial y}+w_z\frac{\partial t}{\partial z}=a\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right); \tag{26-14}$$

the equation of heat transfer at the boundary between a solid and surrounding medium is

$$\alpha\,\Delta t=-\lambda\left(\frac{\partial t}{\partial x}\right)_w. \tag{26-15}$$

Let us write the equations for two similar systems.

The processes of the first system are described by Eqs. (26-12) to (26-15). The processes of the second system are described by the same equations as the processes in the first system, but corresponding quantities have a superscript ($'$). Then

$$\varrho'\left(\frac{\partial w_x'}{\partial \tau'}+w_x'\frac{\partial w_x'}{\partial x'}+w_y'\frac{\partial w_x'}{\partial y'}+w_z'\frac{\partial w_x'}{\partial z'}\right)=$$

$$=\varrho' g_x'-\frac{\partial p'}{\partial x'}+\mu'\left(\frac{\partial^2 w_x'}{\partial x'^2}+\frac{\partial^2 w_x'}{\partial y'^2}+\frac{\partial^2 w_x'}{\partial z'^2}\right); \tag{26-16}$$

$$\frac{\partial w_x'}{\partial x'}+\frac{\partial w_y'}{\partial y'}+\frac{\partial w_z'}{\partial z'}=0; \tag{26-17}$$

$$\frac{\partial t'}{\partial \tau'}+w_x'\frac{\partial t'}{\partial x'}+w_y'\frac{\partial t'}{\partial y'}+w_z'\frac{\partial t'}{\partial z'}=a\left(\frac{\partial^2 t'}{\partial x'^2}+\frac{\partial^2 t'}{\partial y'^2}+\frac{\partial^2 t'}{\partial z'^2}\right); \tag{26-18}$$

$$\alpha'\,\Delta t'=-\lambda'\left(\frac{\partial t'}{\partial x'}\right)_w. \tag{26-19}$$

On the basis of the similarity of the processes the corresponding quantities for the two systems are interrelated in pairs by the similitude transformation factors:

$$\frac{x'}{x}=\frac{y'}{y}=\frac{z'}{z}=C_l; \quad \frac{\tau'}{\tau}=C_\tau;$$

$$\frac{w_x'}{w_x}=\frac{w_y'}{w_y}=\frac{w_z'}{w_z}=C_w; \quad \frac{\varrho'}{\varrho}=C_\varrho; \quad \frac{g'}{g}=C_g;$$

$$\frac{p'}{p}=C_p;\quad \frac{\mu'}{\mu}=C_\mu;\quad \frac{a'}{a}=C_a;$$
$$\frac{\Delta t'}{\Delta t}=\frac{t'}{t}=C_t;\quad \frac{\lambda'}{\lambda}=C_\lambda;\quad \frac{\alpha'}{\alpha}=C_\alpha.$$

Let us express all the variables in Eqs. (26-10) to (26-19) of the second system in terms of the variables of the first system and the similitude transformation factors:

$$\frac{C_\varrho C_w}{C_\tau}\varrho\frac{\partial w_x}{\partial \tau}+\frac{C_\varrho C_w^2}{C_l}\varrho\left(w_x\frac{\partial w_x}{\partial x}+w_y\frac{\partial w_x}{\partial y}+w_z\frac{\partial w_x}{\partial z}\right)=$$
$$=C_\varrho C_g\varrho g_x-\frac{C_p}{C_l}\frac{\partial p}{\partial x}+\frac{C_\mu C_w}{C_l^2}\mu\left(\frac{\partial^2 w_x}{\partial x^2}+\frac{\partial^2 w_x}{\partial y^2}+\frac{\partial^2 w_x}{\partial z^2}\right); \tag{26-20}$$

$$\frac{C_w}{C_l}\left(\frac{\partial w_x}{\partial x}+\frac{\partial w_y}{\partial y}+\frac{\partial w_z}{\partial z}\right)=0; \tag{26-21}$$

$$\frac{C_t}{C_\tau}\frac{\partial t}{\partial \tau}+\frac{C_w C_t}{C_l}\left(w_x\frac{\partial t}{\partial x}+w_y\frac{\partial t}{\partial y}+w_z\frac{\partial t}{\partial z}\right)=\frac{C_a C_t}{C_l^2}a\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right); \tag{26-22}$$

$$C_\alpha C_l\alpha\,\Delta t=-\frac{C_\lambda C_t}{C_l}\lambda\frac{\partial t}{\partial x}. \tag{26-23}$$

The transformation results in the two similar systems being expressed in terms of the variables of the first system. The two systems contain the same variables, determined in the same way. This is possible only when Eqs. (26-12) to (26-15) and Eqs. (26-20) to (26-23) are identical. It follows from the conditions of identity of the equations that the dimensional groups, or complexes, composed of the similarity transformation factors must be equal to one another:

$$\frac{C_\varrho C_w}{C_\tau}=\frac{C_\varrho C_w^2}{C_l}=C_\varrho C_g=\frac{C_p}{C_l}=\frac{C_\mu C_w}{C_l^2} \tag{26-24}$$

Grouping the terms of relationship (26-24) in pairs, we get:

$$\frac{C_\varrho C_w}{C_\tau}=\frac{C_\varrho C_w^2}{C_l},\quad \text{or}\quad \frac{C_w C_\tau}{C_l}=1; \tag{26-25}$$

$$\frac{C_\varrho C_w^2}{C_l}=C_\varrho C_g,\quad \text{or}\quad \frac{C_l C_g}{C_w^2}=1; \tag{26-26}$$

$$\frac{C_\varrho C_w^2}{C_l}=\frac{C_p}{C_l},\quad \text{or}\quad \frac{C_p}{C_\varrho C_w^2}=1; \tag{26-27}$$

$$\frac{C_\varrho C_w^2}{C_l}=\frac{C_\mu C_w}{C_l^2},\quad \text{or}\quad \frac{C_\varrho C_w C_l}{C_\mu}=1. \tag{26-28}$$

Substituting the values of the similitude transformation factors into relationships (26-25) to (26-28) and grouping the terms with respect to the

subscripts, we obtain the following dimensionless terms (criteria of similarity):

$$\mathrm{Ho}=\frac{w\tau}{l}=\text{idem}; \tag{26-29}$$

$$\mathrm{Fr}=\frac{gl}{w^2}=\text{idem}; \tag{26-30}$$

$$\mathrm{Eu}=\frac{p}{\varrho w^2}=\frac{\Delta p}{\varrho w^2}=\text{idem}; \tag{26-31}$$

$$\mathrm{Re}=\frac{\varrho wl}{\mu}=\frac{wl}{\nu}=\text{idem}, \tag{26-32}$$

where Ho = dimensionless term of hydrodynamic homochronicity, characterizing the rate of change with time of the velocity field of a fluid in flow;
Fr = Froude number determining the ratio of intertial forces to forces of gravity;
Eu = Euler number characterizing the ratio of pressure to inertial forces;
Re = Reynolds number representing the ratio of inertial forces to viscosity and determining the pattern of fluid flow.

The criteria of similarity, Ho, Fr, Eu and Re, find application in the study of the hydrodynamic similarity of two or more systems. For any two corresponding points they have the same values.

Equations (26-14) and (26-22) reduce to the following relationships

$$\frac{C_t}{C_\tau}=\frac{C_aC_t}{C_l^2}, \quad \text{or} \quad \frac{C_aC_\tau}{C_l^2}=1; \tag{26-33}$$

$$\frac{C_wC_t}{C_l}=\frac{C_aC_t}{C_l}, \quad \text{or} \quad \frac{C_wC_l}{C_a}=1. \tag{26-34}$$

Replacing the similarity transformation factors by their values and separating the variables, we obtain the following dimensionless terms:

$$\mathrm{Fo}=\frac{a\tau}{l^2}=\text{idem}; \tag{26-35}$$

$$\mathrm{Pe}=\frac{wl}{a}=\text{idem}, \tag{26-36}$$

where Fo = Fourier number, the criterion of similarity for thermal homochronicity, characterizing the relation between the rate of change of the temperature field, the physical parameters and the size of a body;
Pe = Peclet number, the similarity criterion for heat transfer by convection.

Replacing in the Peclet number the thermal diffusivity a by its value, equal to $\lambda/c\varrho$, and multiplying the numerator and the denominator by the

excess temperature ϑ, then $\mathrm{Pe}=\frac{\varrho cw\vartheta}{(\lambda/l)\vartheta}$, i.e. the numerator of the similarity criterion characterizes the heat transported by convection and the denominator—the heat transferred by conduction.

From the heat-transfer Eqs. (26-15) and (26-23) we obtain the following relationship;

$$C_\alpha C_l=\frac{C_\lambda C_t}{C_l}, \quad \text{or} \quad \frac{C_\alpha C_l}{C_\lambda}=1. \tag{26-37}$$

Upon transformation and separation of variables, we obtain

$$\mathrm{Nu}=\frac{\alpha l}{\lambda}=\text{idem}, \tag{26-38}$$

where Nu is the Nusselt number characterizing heat transfer by convection between a fluid and surface of a solid body.

The Nusselt number is determined by the same quantities as the Biot number, but the Nusselt number includes the thermal conductivity of the heat-carrying agent, or fluid, while the Biot number includes the thermal conductivity of the solid.

The Fo, Pe and Nu numbers are used when studying problems involving thermal similarity of two or more systems. For arbitrary corresponding points they have the same values.

Dividing the Peclet number by the Reynolds number, we obtain a new dimensionless term denoted by Pr:

$$\mathrm{Pr}=\frac{\mathrm{Pe}}{\mathrm{Re}}=\frac{\nu}{a}, \tag{26-39}$$

where Pr is the Prandtl number which determine the physical properties of a liquid.

The Peclet number can be represented as the product of the Re and Pr numbers, namely,

$$\mathrm{Pe}=\mathrm{Re}\cdot\mathrm{Pr}=\frac{wl}{\nu}\cdot\frac{\nu}{a}=\frac{wl}{a} \tag{26-40}$$

When studying heat transfer in a free liquid flow, the Froude number is taken into account, but the velocity w must be cancelled from it since it is difficult to measure. To do this, we multiply Fr by Re^2, obtaining

$$\mathrm{Ga}=\mathrm{Fr}\,\mathrm{Re}^2=\frac{gl^3}{\nu^2}=\text{idem}, \tag{26-41}$$

where Ga is the Galilei number characterizing the relation between the forces of gravity and molecular friction.

Multiplying the Ga number obtained by the simplex $(\varrho-\varrho_0)/\varrho_0$, where ϱ and ϱ_0 represent the density of the liquid at two points, we obtain a new dimensionless term

$$\mathrm{Ar}=\mathrm{Ga}\frac{\Delta\varrho}{\varrho_0}=\frac{gl^3}{\nu^2}\cdot\frac{\Delta\varrho}{\varrho_0}, \tag{26-42}$$

where Ar is the Archimedes number determining the conditions of free flow of the medium.

For the case when the change in fluid density is due to the difference between the temperatures at different points of the flow [$\varrho=\varrho_0(1-\beta\Delta t)$], the term $(\varrho-\varrho_0)/\varrho_0$ can be replaced by $\beta\Delta t$, where β is the volumetric expansion coefficient of the medium (for a gas $\beta=1/T$). Then, the Archimedes number turns into a new dimensionless term

$$\mathrm{Gr}=\frac{\beta g l^3 \Delta t}{\nu^2}, \tag{26-43}$$

where Gr is the Grashof number characterizing the relationship between the buoyancy force, arising due to the difference in fluid density, and the forces due to molecular friction.

The dimensionless terms Fr, Ga, Ar and Gr are identical, being four different kinds of the same dimensionless term.

26-5. Criterion Equations

The name *criterion equation* is given to a relationship between any unknown, or variable, dimensionless term and other reference, or dimensionless terms.

In calculations for heat equipment, the unknown quantities are the heat-transfer coefficient α and the pressure drop Δp. Convective heat exchange is characterized by five dimensionless terms, the Nu, Eu, Pr, Gr and Re numbers.

The Nu number constains the unknown heat-transfer coefficient α and the Eu number—the unknown quantity Δp characterizing the hydraulic resistance offered to fluid flow. That is why the Nu and Eu numbers are considered as *unknown* or *dependent* criteria of similarity and the Pr, Gr and Re numbers—as *independent* or *reference criteria* of similarity.

For convective heat transfer the criterion equations can be given in the following form:

$$\mathrm{Nu}=f_1(\mathrm{Re},\ \mathrm{Gr},\ \mathrm{Pr}); \tag{26-44}$$

$$\mathrm{Eu}=f_2(\mathrm{Re},\ \mathrm{Gr},\ \mathrm{Pr}). \tag{26-45}$$

Such a relationship between dimensionless terms is a consequence of the second theorem of similarity.

The relationship between criteria of similarity is usually determined experimentally.

In the case of a fluid in forced flow or in fully-developed turbulent flow, there is little free convection, compared with forced convection. Hence the criterion equation of heat transfer takes a simpler appearance:

$$\mathrm{Nu}=f(\mathrm{Re},\ \mathrm{Pr}). \tag{26-46}$$

For some gases the Prandtl number, Pr, changes only slightly with

temperature in the process of convective heat transfer, and then the criterion equation acquires a still simpler form:

$$\mathrm{Nu}=f(\mathrm{Re}). \tag{26-47}$$

With free fluid flow in the absence of forced convection the Reynolds number in the criterion equation of heat transfer must be replaced by the Grashof number. Then we obtain

$$\mathrm{Nu}=f(\mathrm{Gr},\ \mathrm{Pr}). \tag{26-48}$$

Experimental studies of heat transfer in liquids have shown that the heat-transfer coefficient α is not the same in conditions of heating and cooling. This phenomenon is associated with the changes in the physical properties of a liquid in the boundary layer. In order to derive criterion equations equally valid for both heating and cooling, the following supplementary relationships are introduced:

$$\frac{t_f}{t_w},\quad \frac{\mu_f}{\mu_w},\quad \frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}.$$

The first ratio is usually used when calculating heat transfer in gases, and the remaining two—when calculating heat transfer in liquids.

The Soviet academician M. A. Mikheyev recommended taking the direction of heat flow into account by using the ratio $\mathrm{Pr}_f/\mathrm{Pr}_w$ raised to the power 0.25. Then, the general criterion equation of convective heat transfer takes the following form:

$$\mathrm{Nu}=c\,\mathrm{Re}^n\cdot\mathrm{Gr}^b\cdot\mathrm{Pr}^m\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)0.25. \tag{26-49}$$

All equations describing particular cases of convective heat transfer may be put in this form. The quantitative relationship between dimensionless terms is the object of experimental investigations.

26-6. Simulation (Modelling) of Convective Heat Transfer

The experimental investigation of various physical phenomena in general and of thermal phenomena in particular can be done by directly using full-scale equipment or by using scale models. The conditions of simulation, i.e. the conditions to be satisfied by the scale model, and the process taking place in it are given by the theory of similarity. The possibilities of applying the theory of similarity to experimental studies are almost unlimited.

In the preceding sections it was established that all the similar phenomena of some group of phenomena represent one and the same phenomenon to different scales. The conclusions drawn in studying any phenomenon of a group can be applied to all phenomena of the group. Consequently, the study of a particular phenomenon from a given group of phenomena is equivalent to the study of any other phenomenon from the same group. So whenever direct experimental study of a particular phenomenon in

full-size pilot equipment (or apparatus) is hampered because of technical or economical reasons, then a similar phenomenon is investigated in a scale model.

By *simulation*, or *modelling*, is meant a method of experimental investigation in which some physical phenomenon is studied in a smaller scale model. The idea of simulation stems from the fact that any phenomenon described by dimensionless variables reflects the characteristics of a group of similar phenomena.

For a model to be similar to full-size pilot equipment the following conditions must be fulfilled. Processes that can be simulated must have the same physical nature and be described by the same differential equations. The conditions of unambiguity must be the same in all respects, except the numerical values of the constants present in them. *The conditions of unambiguity require* the geometrical similarity of the full-size pilot equipment and the scale model; similarity of the conditions of fluid flow in the inlet sections of the full-size pilot equipment and the scale model; similarity of the physical parameters at corresponding points in the full-size pilot equipment and the model; similarity of the temperature fields on the boundaries of the fluid medium. In addition, like reference (independent) dimensionless terms at corresponding sections of the full-size equipment and the scale model must be numerically equal.

The above conditions of similarity for the full-scale pilot equipment and the scale model are necessary and sufficient. However, in practice, precise implementation of all conditions of simulation is difficult. Hence methods of approximate simulation have been developed, comprising the stability and self-similarity of flow and involving the use of the *method of locality*, also known as the *method of local thermal simulation.*

It is not difficult to ensure geometric similarity between full-size pilot equipment and its scale model. Similar velocity distribution in the entry section can also be realized comparatively simply. The similarity of physical parameters in the flow of fluid through a model and full-size pilot equipment can be realized only approximately, and it is also difficult to ensure the similarity of the temperature fields at the heating surfaces in the scale model and full-size pilot equipment. For this use is made of the approximate method of local thermal simulation.

Local thermal simulation is the realization of the similarity of the temperature fields not over the entire volume of the apparatus, but in the places where local heat transfer is being investigated. The requirement of equality of the reference dimensionless terms in the full-size pilot equipment and scale model can be fulfilled approximately.

By *stability* is meant the property whereby a viscous liquid always acquires at some distance from the inlet section the same velocity distribution over the cross section of the conduit, irrespective of the velocity distribution at the inlet section.

By the phenomenon of self-similarity is meant the phenomenon exhibited by a fluid flow whereby the velocity distribution over a given cross section

(of the conduit) scarcely changes for a fairly wide range of velocities, i.e. it practically ceases to depend on Re.

These days simulation is one of the fundamental methods of scientific research and is widely practised in many branches of science and engineering. It has become a powerful means of detecting various defects in existing technological facilities and of finding ways of eliminating them. In addition, simulation is now widely used to check newly designed apparatus, making it possible to improve designs not yet constructed.

Typical Questions to Chapter Twenty Six

1. What is meant by convective heat exchange?
2. What kinds of convection are distinguished?
3. Discuss dynamic and thermal boundary layers and their physical meaning.
4. What patterns of fluid flow are encountered and what is the difference between them?
5. Discuss Reynolds number and its notation.
6. What is the dimensionality of the Reynolds number?
7. What is the critical value of the Reynolds number?
8. What is the mechanism of heat transfer with the laminar and turbulent patterns of fluid flow?
9. Give a definition of dynamic and kinematic viscosity.
10. What factors influence convective heat transfer?
11. Give the definition of the (local) heat-transfer coefficient.
12. On what quantities does the heat-transfer coefficient depend?
13. Write down the system of differential equations for heat transfer by convection.
14. What is meant by conditions of unambiguity?
15. Why is the theory of similarity used to determine the heat-transfer coefficient?
16. What conditions form the basis for the theory of similarity?
17. On what quantities does the heat-transfer coefficient depend?
18. State the three theorems of similarity.
19. What differential equations are used to obtain dimensionless terms (criteria of similarity)?
20. What dimensionless terms are obtained from the differential equations for convective heat transfer?
21. What equation is called a criterion equation?
22. What dimensionless terms characterize heat transfer by convection in gases and liquids?
23. What ratio takes into account the direction of heat flow?

CHAPTER TWENTY SEVEN

HEAT TRANSFER BY CONVECTION WITH FLUID IN FORCED AND FREE FLOW*

27-1. Mean (Average) Temperature. Reference Temperature. Equivalent Diameter

All formulae for calculation which of the magnitude of a heat flux include the temperature of the fluid, which is usually distributed nonuniformly both over the cross-section of the channel and along its length. Accordingly, in engineering calculations what is meant by the temperature of fluid is the mean or average temperature of the flow, which is determined in the following way.

A flow of fluid carries through an elementary area dF per unit time an amount of heat

$$dQ = c_p \varrho t w \, dF.$$

The amount of heat transferred through the given cross section per unit time is determined by formula

$$Q = \int_F c_p \varrho t w \, dF.$$

Dividing the above expression by $\int_F c_p \varrho w \, dF$, we obtain the mean temperature over the cross section (taken with respect to fluid enthalpy)

$$t_m = \frac{\int_F \varrho c_p w t \, dF}{\int_F \varrho c_p w \, dF}. \tag{27-1}$$

Since the dependence of c_p and ϱ on temperature can usually be ignored, Eq. (27-1) takes the form

$$t_m = \frac{\int_F t w \, dF}{\int_F w \, dF} = -\frac{1}{V} \int_F w t \, dF, \tag{27-2}$$

where F = cross-sectional area of the channel, m²;
t = fluid temperature in each element of the section, deg;

* Since this textbook is intended for students not specializing in power engineering, no theoretical explanations or charts for forming criterion equations are given in this chapter. A detailed treatment of these problems can be found in [4].

V = volumetric rate of fluid flow, m^3/s;
w = fluid velocity in each elementary area dF.

If the fluid flow velocity is constant along the channel or equal to zero, then Eq. (27-2) acquires the appearance

$$t_m=\frac{1}{F}\int_F t\,dF.$$

The fluid temperature at individual points of the channel over its cross section can be measured by thermocouples.

If fluid temperature varies not only over the cross section of the channel but also along its length, the temperature must also be averaged along the flow of the fluid. Let us denote the initial temperature of the wall by t'_w, the mean temperature of the fluid at the inlet to the channel by t'_2 and at the outlet from the channel by t''_2, then the averaged temperature t_f, of the fluid along the channel can be determined by formula

$$\bar{t}_f=\frac{t'_w+t''_w}{2}\pm\frac{(t'_2-t'_w)-(t''_2-t''_w)}{\ln\dfrac{t'_2-t'_w}{t''_2-t''_w}}, \tag{27-3}$$

where $(t'_2-t'_w)$ and $(t''_2-t''_w)$ are the temperature differences in the initial and final sections of the channel.

In formula (27-3) the plus sign is taken when the fluid is cooled, and the minus sign—when fluid is heated. For the simplest cases when the fluid temperature varies within a narrow range, the mean temperature can be taken to be the arithmetic mean of the extreme values

$$\bar{t}_f=0.5(t'+t''). \tag{27-4}$$

In all the criterion equations given below the heat-transfer coefficient is always determined by the mean fluid velocity

$$\bar{w}_m=\frac{1}{F}\int_F w\,dF=\frac{V}{F}. \tag{27-5}$$

The physical parameters of gases and liquids vary with temperature. Thus when treating experimental results the mean temperature of the fluid or wall, or the mean temperature of the boundary layer is chosen as the reference temperature, from which the values of the physical properties are taken

$$\bar{t}_{b\,l}=0.5(t_w+t_f).$$

When determining the heat-transfer coefficients it is always necessary to note which temperature is taken as the reference temperature for a given criterion equation.

Some criterion equations include a linear dimension that affects the development of the process investigated. When dealing with tubes with circular cross-section the linear reference dimension is the inside diameter

of the tube. For channels with a non-circular cross section the inside diameter is replaced by the so-called *equivalent diameter* $d_{eq}=4F/S$, where F is the cross-sectional area of the conduit, and S the full (wetted) perimeter of the cross section irrespective of which part of it takes part in heat transfer.

When a tube or bank of tubes is exposed to cross flow the outside diameter of the tube is taken as the reference dimension. When a plate is exposed to fluid flow the reference dimension for it is the length of the plate in the direction of flow. In general, when using criterion equations, attention should be paid to the dimension used as the reference dimension in the dimensionless terms.

27-2. Heat Transfer in Laminar Fluid Flow in Tubes

The mechanism of the heat-transfer process when fluid flows along straight smooth tubes is very intricate.

The intensity of heat transfer may vary within wide limits and depends to a great extent on the velocity of flow.

Fluid temperature varies both over the cross section of the tube and along the length of the tube.

Then pattern of fluid flow in tubes may be laminar or turbulent. The pattern of flow is determined by the magnitude of the Reynolds number: $\mathrm{Re}=\bar{w}d/\nu$ where $\bar{w}$ is the mean fluid velocity; d is the inside tube diameter; ν is the kinematic viscosity. When $\mathrm{Re}<2\times10^3$ fluid is said to be in laminar flow. When $\mathrm{Re}=2\times(10^3-10^4)$ the pattern of flow is referred to as *transition flow*. At $\mathrm{Re}>10^4$ fully-developed turbulent fluid flow sets in. The pattern of flow forms in the initial section of the tube. At the inlet to the tube there is uniform distribution of velocity over the cross section of the tube. Then, as the fluid flows along the tube a hydrodynamic boundary layer forms at the walls of the tube whose thickness gradually increases till it becomes equal to the radius of the tube, and a constant velocity distribution ensues in the tube characteristic of the given pattern of flow. *Stabilized flow* is then said to take place. The latter phenomenon is observed with fluid in both laminar and turbulent flow. The length of the stabilized-flow section is about 50 d.

Theoretical and experimental studies have shown that heat transfer with fluids in flow along tubes varies along the tube, so in addition to the stabilized-flow section, a section of thermal stabilization, $l_{s\,th\,st}$, forms. At the inlet to the tube the heat-transfer coefficient α assumes its maximum value, then it drops abruptly and along the section of stabilized flow $l_{st\,f}$, it tends to a constant value (Fig. 27-1). The thickness of the thermal boundary

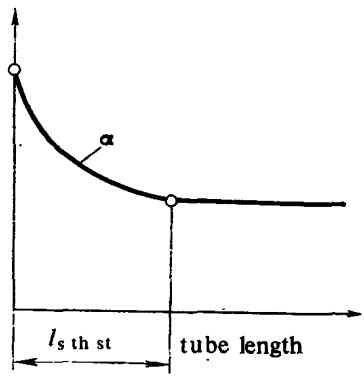


FIG. 27-1

layer forming at the surface of the tube increases with the distance from the inlet to the tube until on the section of thermal stabilization it equals the radius of the tube. The length of the stabilized-flow section of a horizontal round tube depends on many quantities—the thermal conductivity, the Reynolds number, the stabilized flow and others, and is assumed equal to 50 *d*.

With fluid in isothermal laminar flow along a tube, the velocity distribution over the cross section is parabolic as shown in Fig. 27-2*a*, the velocity at a distance of r_x from the tube axis being

$$w = w_{max}\left(1 - \frac{r_x^2}{r^2}\right),$$

where w_{max} = fluid velocity at the tube axis (at $r_x = 0$);
r = tube radius.

The velocity is maximum at the tube axis and equal to zero at the wall.

For laminar flow the mean velocity $\bar{w} = 0.5 w_{max}$.

With laminar fluid flow two patterns of non-isothermal flow are distinguished: viscous and viscous-gravitational. The two patterns of non-isothermal flow obey different laws.

Viscous flow occurs when a viscous fluid flows in the absence of natural convection, with heat being transferred to or from the walls of the tube only by conduction.

The viscous-gravitational pattern of flow takes place when forced fluid flow is accompanied by natural (free) convection, with heat transfer being then due not only to conduction, but also to convection.

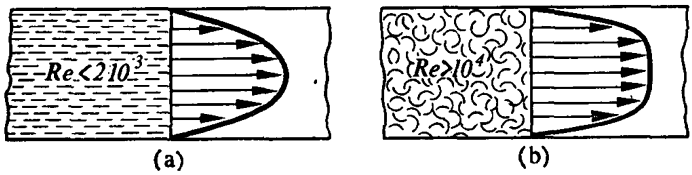
With a fluid in viscous flow, the velocity distribution over the cross section of the conduit is not purely parabolic since a change in temperature over the cross section also causes a change in fluid viscosity. It should be emphasized here that the velocity of distribution depends on the direction of heat flow. When a fluid is heated its temperature at the wall is higher than that of the bulk of the fluid, and its viscosity is less; upon cooling the situation is reversed. So, when a fluid is heated the velocities at the wall are higher than in the case of cooling and the intensity of heat transfer is greater.

For viscous-gravitational flow the direction of natural convection and forced convection is very important. These directions may coincide, or the free convection and forced convection may be oppositely directed, or, as is observed in horizontal tubes, they may be mutually perpendicular.

When natural and forced convection are in the same direction the fluid velocity at the wall rises and the rate of heat transfer increases. When natural and forced convection are oppositely directed the velocities at the wall decrease and the rate of heat transfer drops, but sometimes there are cases when vortex motion forms at the wall and this may cause a higher rate of heat transfer.

When forced and natural convection flows are mutually perpendicular the rate of heat transfer increases due to better mixing of the fluid.

Thus, no strictly laminar flow can exist under non-isothermal conditions.



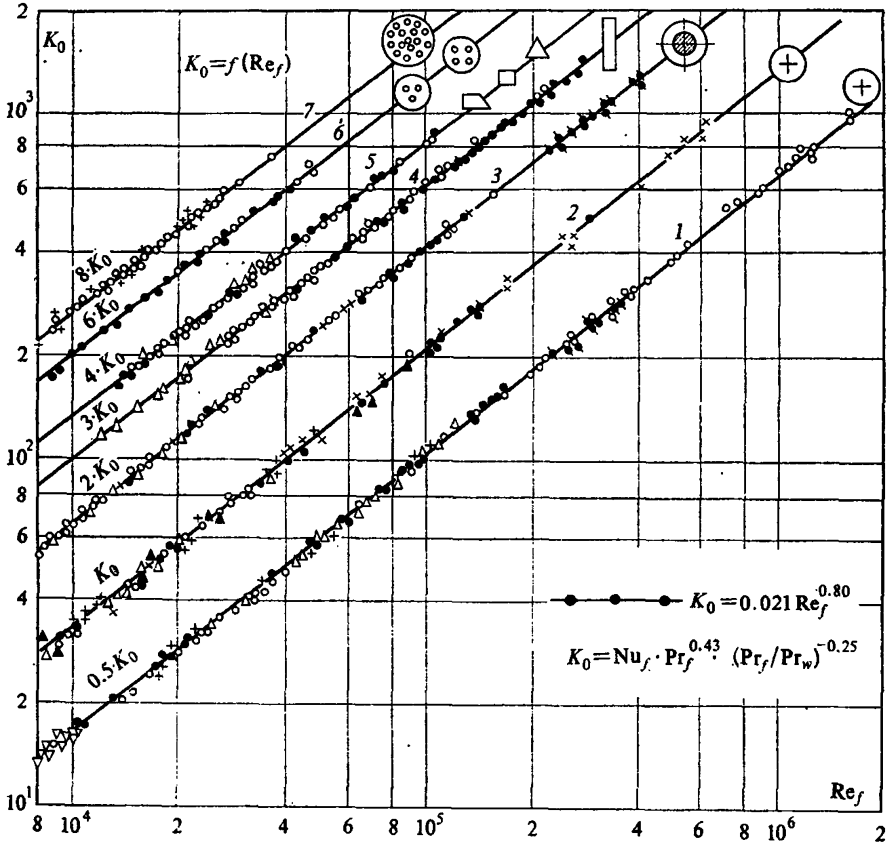


FIG. 27-2

Analytical studies of heat transfer in laminar flow have not yet yielded conclusive results and the local heat-transfer coefficient α is determined by empirical formulae.

In the event of viscous flow M. A. Mikheyev recommends calculating the average heat-transfer coefficient for fluids flowing along straight smooth tubes by the formula

$$\overline{\mathrm{Nu}}_{fd}=0.15\ \mathrm{Re}_{fd}^{0.33}\ \mathrm{Pr}_f^{0.43}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}. \qquad (27\text{-}6)$$

For viscous-gravitational flow quite precise generalizations of test results were obtained by M. A. Mikheyev, who recommended the following approximation for the mean heat-transfer coefficient for fluid in flow in straight smooth tubes

$$\overline{\mathrm{Nu}}_{fd}=0.15\ \mathrm{Re}_{fd}^{0.33}\ \mathrm{Pr}_f^{0.43}\ \mathrm{Gr}_{fd}^{0.1}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}. \tag{27-7}$$

For air the formula simplifies and takes the form

$$\overline{\mathrm{Nu}}_{fd}=0.13\ \mathrm{Re}_{fd}^{0.33}\ \mathrm{Gr}_f^{0.1}. \tag{27-8}$$

These equations are used to determine the Nusselt number which gives the heat-transfer coefficient $\bar{\alpha}=\overline{\mathrm{Nu}}\,\lambda/d$, where the average temperature of the fluid is taken as reference temperature; the reference velocity is the average fluid flow velocity in the tube; and the reference dimension is the diameter in the case of a round tube or the equivalent diameter for a conduit of any shape. These formulae give the value of the mean heat-transfer coefficient when $l/d>50$. They are applicable to any fluid and fully allow for the influence of natural convection and direction of heat flow. The latter is taken into account by the raising of the ratio of the Prandtl number for the fluid and wall to the 0.25 power.

For air and diatomic gases the Prandtl number is practically independent of temperature, therefore the ratio $\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}=1$.

TABLE 27-1

Value of $\bar{\varepsilon}_l$ for Laminar Flow

l/d	1	4	5	10	15	20	30	40	50
$\bar{\varepsilon}_l$	1.9	1.7	1.44	1.28	1.18	1.13	1.05	1.02	1.0

For tubes of a length $l<50d$ the heat-transfer coefficient α calculated by formulae (27-6) to (27-8) must be multiplied by a mean correction factor $\bar{\varepsilon}_l$ taken from Table 27-1.

27-3. Heat Transfer in Turbulent Fluid Flow in Tubes

When a fluid is in turbulent flow in a tube it is not possible to describe the distribution of velocity by one equation, because of the more intricate structure of flow. Almost the entire cross section of the tube is filled with the turbulent flow and it is only at the wall that a laminar sublayer forms. This offers the main thermal resistance. With stabilized turbulent flow the curve representing velocity distribution over a cross section takes the form of a truncated parabola, as shown in Fig. 27-2*b*. The fluid velocity curve changes sharply near the wall within the boundary layer, while it slopes

gently at the central part of the cross section. Maximum flow velocity is observed at the tube axis. Practical calculations are done with mean velocities

$$\bar{w}=\frac{V}{F},$$

where V = rate of fluid flow, m^3/s;
F = cross-sectional area of the tube, m^2.

With turbulent flow the ratio of the mean velocity to the maximum is a function of the Reynolds number

$$\frac{\bar{w}}{w_{max}}=f(\mathrm{Re})\approx 0.8-0.9.$$

The above relationships for the turbulent flow of a fluid are only valid for isothermal flow.

With turbulent flow the fluid is mixed intensively, and natural convection has almost no effect on heat transfer. Hence the Grashof number can be removed from the set of independent dimensionless terms. The fluid temperature over the cross section of the core is practically constant. When a fluid is being heated the intensity of heat transfer is higher than upon cooling. This dependence is accounted for by the ratio

$$\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}.$$

For developed turbulent flow ($\mathrm{Re}_{fd}>10^4$), when $\frac{l}{d}>50$, as academician M. A. Mikheyev recommends that the mean heat-transfer coefficient be determined from the following criterion equation

$$\overline{\mathrm{Nu}}_{fd}=0.021\ \mathrm{Re}_{fd}^{0.8}\ \mathrm{Pr}_f^{0.43}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25} \qquad (27\text{-}9)$$

For air ($\mathrm{Pr}\approx 0.7$) this formula takes a simpler form

$$\overline{\mathrm{Nu}}_{fd}=0.018\ \mathrm{Re}_{fd}^{0.8}. \qquad (27\text{-}10)$$

Here the reference temperature is the mean temperature of fluid and the reference dimension is the diameter for a round tube or the equivalent diameter for conduit of arbitrary shape. The formulae are applicable within the following limits:

$$\mathrm{Re}_{fd}=1\times 10^4-5\times 10^6 \quad \text{and} \quad \mathrm{Pr}_f=0.6-2500.$$

For tubes with a ratio $l/d<50$ the heat-transfer coefficient is higher, therefore the value of $\bar{\alpha}$ calculated with the aid of formulae (27-9) and (27-10) must be multiplied by the mean correction factor $\bar{\varepsilon}_l$ (Table 27-2). Test results are given in Fig. 27-2*c*.

With fluid in turbulent flow in curved tubes, coils or loops, the centrifugal forces appearing in the fluid create the so-called secondary circulation over the cross section of the tube, resulting in a higher heat-transfer coefficient.

TABLE 27-2

Values of $\bar{\varepsilon}_l$ for Turbulent Flow

l/d	$\bar{\varepsilon}_l$ at				
	$Re=1\times10^4$	$Re=2\times10^4$	$Re=5\times10^4$	$Re=1\times10^5$	$Re=1\times10^6$
1	1.65	1.51	1.34	1.28	1.14
2	1.50	1.40	1.27	1.22	1.11
5	1.34	1.27	1.18	1.15	1.08
10	1.23	1.18	1.13	1.10	1.05
15	1.17	1.13	1.10	1.08	1.04
20	1.13	1.10	1.08	1.06	1.03
30	1.07	1.05	1.04	1.03	1.02
40	1.03	1.02	1.02	1.02	1.01
50	1	1	1	1	1

Heat transfer in coils must be calculated using Eqs. (27-9) and (27-10) derived for straight tubes, but the heat-transfer coefficient α obtained must be multiplied by the correction factor $\bar{\varepsilon}_{coil}=1+3.6\frac{d}{D}$, where d is the diameter of the tube, m, and D—the diameter of the spiral. In coils the effect of secondary circulation propagates along the entire length of the curved tube.

27-4. Heat Transfer in Transition Flow

The transition pattern of fluid flow is observed in channels at $Re=2\times10^3-2\times10^4$. Heat transfer in this case depends on many factors difficult to account for and so cannot be described by just one criterion equation. The above equations derived for laminar and turbulent patterns of flow cannot be applied to the transition pattern of flow.

In Fig. 27-3 the dimensionless group K_0 or the transition pattern of flow is plotted as a function of the Reynolds number Re. As can be seen from the diagram in the region of transition flow, the experimental points cannot be described by a single relationship. The intensity of heat transfer rises sharply with Re, while the rate of heat exchange is influenced by natural convection whose extent is measured by the Grashof number. The greater the Grashof number, the larger is the dimensionless group K_0 and so the larger is the heat-transfer coefficient α. With developed turbulent flow ($Re\approx10^4$) all curves merge into one line.

Due to the fact that no satisfactory method for calculating the heat transfer in the transition zone has yet been devised, the heat-transfer coefficient can only be approximately determined with the aid of the criterion equation

$$K_0=Nu_{f\,d}\,Pr_f^{-0.43}\left(\frac{Pr_f}{Pr_w}\right)^{-0.25}.$$

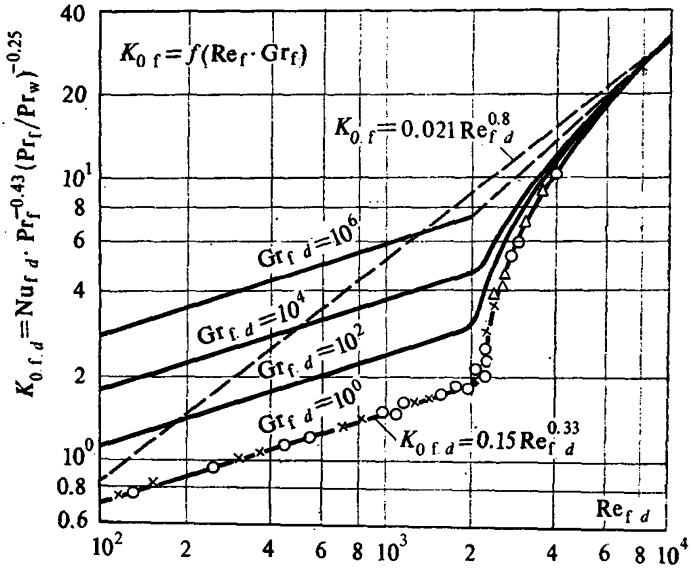


FIG. 27-3

The maximum values of the dimensionless group $K_{0\,max}$ can be obtained from the criterion equation for turbulent flow in tubes, and the minimum values of the dimensionless group $K_{0\,min}$—directly from the chart (without having to allow for the influence of free convection).

27-5. Heat Transfer for a Plate in Forced Longitudinal Flow

If the flat surface of a plate is exposed to an infinite fluid flow with a uniform velocity distribution, then a hydrodynamic boundary layer forms on it, starting at the front edge of the plate. In the hydrodynamic boundary layer, due to the presence of friction the fluid velocity varies from the velocity of free-stream flow to zero. In the boundary layer fluid flow may be both laminar and turbulent (Fig. 26-2).

It has been shown experimentally that the change from laminar to turbulent flow does not occur instantaneously, but gradually along some section, the flow in which is referred to as being *transitional.*

The pattern of flow in the boundary layer is judged by the magnitude of the Reynolds number. Thus, laminar flow for a fluid in the boundary layer takes place in isothermal streams when $\mathrm{Re}_{fl}^{*}<5\times10^5$, and in non-isothermal streams—when $\mathrm{Re}_{fl}<4\times10^4$, and destruction of the laminar layer depends on the degree of turbulence of the free-stream flow. If the fluid and the plate

* The subscripts "f" and "l" indicate that the values of the Re are taken by the temperature of the fluid and length of the plate in the direction of flow.

are at different temperatures, in addition to the hydrodynamic boundary layer, a thermal boundary layer forms at the surface of the plate, as shown in Fig. 26-3. Within the thermal boundary layer, the fluid temperature varies from the temperature of the flow at a distance from the plate, to a temperature equal to the surface temperature of the plate.

An analysis of test results shows the heat-transfer coefficient to depend not only on the pattern of fluid flow (laminar or turbulent), but also on the kind of fluid, its temperature, temperature difference and the direction of heat flow, which are a function of temperature. Of the change of fluid viscosity in the boundary layer is also important. In addition, at low flow velocities heat transfer is greatly influenced by natural convection. Since the influence exerted by all these factors on heat transfer is not yet sufficiently clearly understood, it is advisable to determine the mean heat-transfer coefficient for a flat plate in forced longitudinal laminar fluid flow with the aid of the following formulae suggested by M. A. Mikheyev at Reynolds numbers $<4\times10^4$

$$\overline{\mathrm{Nu}}_{fl}=0.66\ \mathrm{Re}_{fl}^{0.5}\ \mathrm{Pr}_f^{0.43}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}. \tag{27-11}$$

For air at $\mathrm{Re}<4\times10^4$ the formula reduces to

$$\overline{\mathrm{Nu}}_{fl}=0.57\ \mathrm{Re}_{fl}^{0.5}. \tag{27-12}$$

In formulae (27-11) and (27-12) the reference temperature is taken to be the temperature of the free-stream flow (Pr_w is taken by the temperature of the wall); the reference velocity is that of the free-stream flow, and the length of the plate in the direction of flow is taken to be the reference dimension. The influence of natural convection on heat transfer is ignored in these formulae, as the problem requires further investigation.

At the turbulent hydrodynamic boundary layer at the surface of the plate, a thin layer of fluid in laminar flow forms, called the laminar sublayer, in which the main change in flow velocity takes place, as well as all the changes of the temperature of the flowing fluid, i.e. the laminar sublayer presents the main hydrodynamic and thermal resistance.

At the present time heat transfer by convection is usually calculated from experimental (empirical) formulae. The coefficient of heat transfer in liquids flowing past a flat plate in the presence of a turbulent boundary layer can be calculated using the formulae recommended by M. A. Mikheyev at $\mathrm{Re}_{fl}>4\times10^4$

$$\overline{\mathrm{Nu}}_{fl}=0.037\ \mathrm{Re}_{fl}^{0.8}\ \mathrm{Pr}_f^{0.43}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}. \tag{27-13}$$

For air at $\mathrm{Pr}\approx0.7$ Eq. (27-13) takes the simpler form

$$\overline{\mathrm{Nu}}_{fl}=0.032\ \mathrm{Re}_{fl}^{0.8}. \tag{27-14}$$

Here the reference temperature is the temperature of the fluid at a distance

from the plate; the length of the plate in the direction of flow is taken as the reference dimension.

It has been shown experimentally that with developed turbulent fluid flow heat transfer is independent of the Grashof number; and hence the entire heat is transported not by natural, but by forced convection.

27-6. Heat Transfer for a Single Tube in Cross Flow

The process of heat transfer for a single round tube in cross fluid flow has a number of peculiarities. Smooth, unseparated flow of fluid past a tube round takes place only at $Re<5$ (Fig. 27-4). With $Re>5$ the pattern of fluid flow past the front half of the tube differs greatly from that past the rear half of the tube (Fig. 27-5). The laminary boundary layer forming at the front half of the tube, near the vertical diameter, separates from the surface of the tube and two symmetrical eddies form at the rear half of the tube. The fluid covers fully only 45 to 47 per cent of the tube surface, at angles $\varphi=80-85°$, measured from the front point. The rest of the tube surface is exposed to eddies. The greater the velocity of flow, the more pronounced the separation of the laminar boundary layer at large angles φ. When the Reynolds number is large the laminar boundary layer becomes turbulent, and the layer separates at $\varphi=120-130°$. Such a shift results in a reduced eddy zone

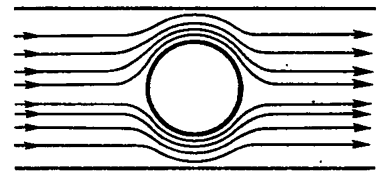


FIG. 27-4

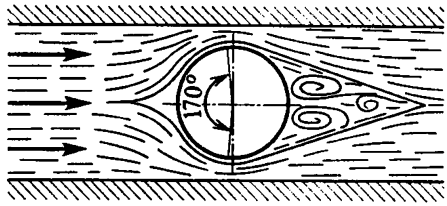


FIG. 27-5

in the rear half of the tube and the greater part of its surface becomes exposed to unseparated fluid flow. The turbulent boundary layer appears at considerable Reynolds numbers, $Re=1\times10^5-4\times10^5$. The appearance of the turbulent boundary layer is greatly influenced by the initial turbulence of flow; the greater the turbulence, the smaller are the Reynolds numbers for which the turbulent boundary layer originates. Such a peculiar pattern of fluid motion past a single tube placed in cross flow influences to a great extent the heat-transfer coefficient over the circumference of the tube.

The heat-transfer coefficient is maximum in the front half of the tube (at $\varphi=0$), since the boundary layer there has minimum thickness. As the

fluid flows past the surface of the tube the thickness of the boundary layer increases and reaches its maximum value at the equator, approximately at the spot where the boundary layer separates from the tube (Fig. 27-6). Due to the increase in the thickness of the boundary layer the heat-transfer coefficient decreases and becomes a minimum at the equator. The rear half of the cylinder is exposed to fluid in complex eddy flow, the boundary layer deteriorates, its thickness diminishes and the heat-transfer coefficient increases, reaching a maximum value at $\varphi=180°$. The intensity of heat transfer here may become equal to that at the front half of the tube. The above pattern of fluid flow past a single round tube in cross flow is valid for Reynolds numbers $Re=(5\text{-}2)\times10^5$. The process of heat transfer for a round tube at $Re>2\times10^5$ has not been investigated well enough and our knowledge of the eddy zone is limited.

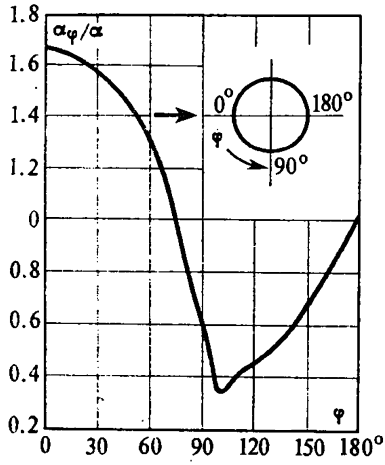


FIG. 27-6

It follows from the foregoing that the process of heat transfer over the circumference of a single tube in cross flow is closely associated with the nature of fluid flow past its surface, and depends on the velocity and direction of fluid flow, on the temperature and diameter of the tube, on the direction of heat flow, on external objects changing the degree of turbulence of the flow, etc. All these factors reflect the difficulties involved in obtaining a theoretical solution of the problem.

Comprehensive experimental investigations of heat transfer for wires and small-diameter tubes placed into cross flow of air, water and transformer oil have been conducted by A. A. Zhukauskas, making use of the experimental results obtained by other researchers. A generalization of all test results made it possible to work out criterion equations for the circumferential mean heat-transfer coefficient in the case of a single tube

at $Re_{fd}=(5\text{-}1)\times10^3$

$$\overline{Nu}_{fd}=0.5\,Re_{fd}^{0.5}\,Pr_f^{0.38}\left(\frac{Pr_f}{Pr_w}\right)^{0.25}; \tag{27-15}$$

for air

$$\overline{Nu}_{fd}=0.43\,Re_{fd}^{0.5}. \tag{27-16}$$

At $Re_{fd}=1\times10^3\text{-}2\times10^5$

$$\overline{Nu}_{fd}=0.25\,Re_{fd}^{0.6}\,Pr_f^{0.38}\left(\frac{Pr_f}{Pr_w}\right)^{0.25}; \tag{27-17}$$

for air

$$\overline{\mathrm{Nu}}_{fd}=0.216\,\mathrm{Re}_{fd}^{0.6}. \qquad (27\text{-}18)$$

In calculating the dimensionless terms, the outside diameter of the tube is taken as the reference linear dimension, the mean fluid temperature is taken as the reference temperature. The velocity is that at the narrowest cross section of the channel.

TABLE 27-3

Values of ε_ψ for a Single Tube

ψ, deg	90	80	70	60	50	40	30	20	10
ε_ψ	1	1	0.98	0.95	0.87	0.77	0.67	0.6	0.55

Formulae (27-15) to (27-18) are valid for a cylinder placed perpendicular to the direction of flow. When the angle of attack $\psi<90°$, the heat-transfer coefficient for $\psi=90°$ must be multiplied by the correction factor $\varepsilon\psi$, taken from Table 27-3, and $\bar{\alpha}_\psi=\varepsilon_\psi\bar{\alpha}_{90°}$.

27-7. Heat Transfer in Fluid Flow Across Banks of Tubes

The complex hydrodynamic nature of fluid flow past a single tube becomes even more intricate when the fluid flows past a bank of round tubes. Heat exchangers, consisting of a bank of round tubes exposed to a fluid flowing past them, are widely used in engineering. Tubes are usually arranged in banks in either an in-line or in a staggered manner, called in-line (Fig. 27-7*a*) or staggered (Fig. 27-7*b*) arrangements.

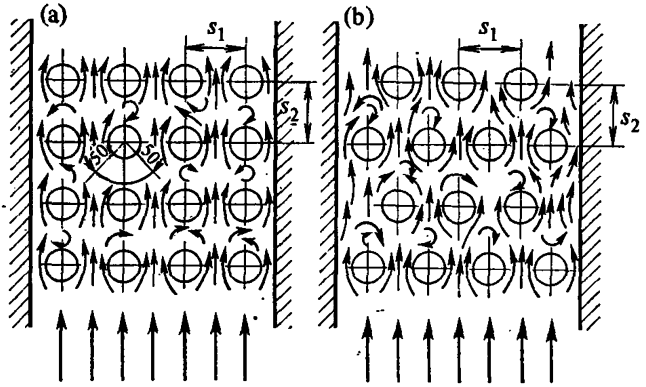


FIG. 27-7

A bank of tubes is characterized by the outside tube diameter, the number of rows of tubes in the direction of fluid flow, and their relative pitches. The ratio of the transverse pitch s_1, i.e. the distance between the axes of the tubes across the bank of tubes (in the direction transverse to the flow) to tube diameter is s_1/d, and the ratio of the longitudinal pitch s_2, which is the distance between the axes of two adjacent rows of tubes in the direction of fluid flow, to the tube diameter is s_2/d. The arrangement of tubes determines to a great extent the pattern of fluid flow, the flow of fluid past each row and the heat transfer in the bank as a whole.

If fluid is in turbulent flow in a channel, the pattern of fluid flow across a bank of tubes will also be turbulent, with the degree of turbulence increasing from row to row, since the bank of tubes is a very good generator of turbulence. If fluid is in laminar flow in the channel upstream of the bank of tubes, then, depending on the Re number, fluid flow across the bank may be both laminar and turbulent.

With small values of the Reynolds number, $Re < 1 \times 10^3$, laminar flow may also be preserved in the bank of tubes. In heat exchangers the fluid is usually in turbulent flow. However when there is turbulent flow the process of heat transfer in the banks of tubes is governed by different laws. The change in the laws governing heat transfer due to the appearance of a turbulent boundary layer on the tubes in the bank, which may occur when $Re \approx 1 \times 10^5$.

At $Re = 1 \times 10^5$ the front part of a tube is exposed to a laminar boundary layer, and the rear part is in an eddy zone, with the fluid being in turbulent flow in the spaces between the tubes. Such a pattern of flow is referred to as *mixed flow*. This pattern of mixed fluid flow, corresponding to Reynolds numbers from $Re = 1 \times 10^3$ to $Re = 1 \times 10^5$, is at present the one best investigated. Let us consider the peculiarities of this pattern of mixed flow. Irrespective of the arrangement of tubes in a bank, the flow of fluid past the tubes of the first row is practically the same as fluid flow past a single tube and the pattern of flow depends only on the initial turbulence of flow. The nature of fluid flow past the subsequent rows of tubes is different in both in-line and staggered banks.

With an in-line arrangement the tubes of any row are shaded by corresponding tubes of the preceding row, which reduces the exposure of the front part, and a great fraction of the tube surface is positioned in the weak eddy zone. In staggered banks no tubes are obstructed by other tubes, so that, under otherwise identical conditions, the heat-transfer coefficient for staggered banks of tubes is higher than that for in-line banks.

Figs. 27-8*a* and *b* show the distribution of the local heat-transfer coefficient over the tube circumference, as a function of the angle φ, for the first and subsequent rows of seven-row in-line and staggered banks of tubes. The values of the relative heat-transfer coefficient $\frac{\alpha_\varphi}{\bar{\alpha}}$ are plotted along the y-axis, and the angle φ measured from the front point of a tube is plotted along

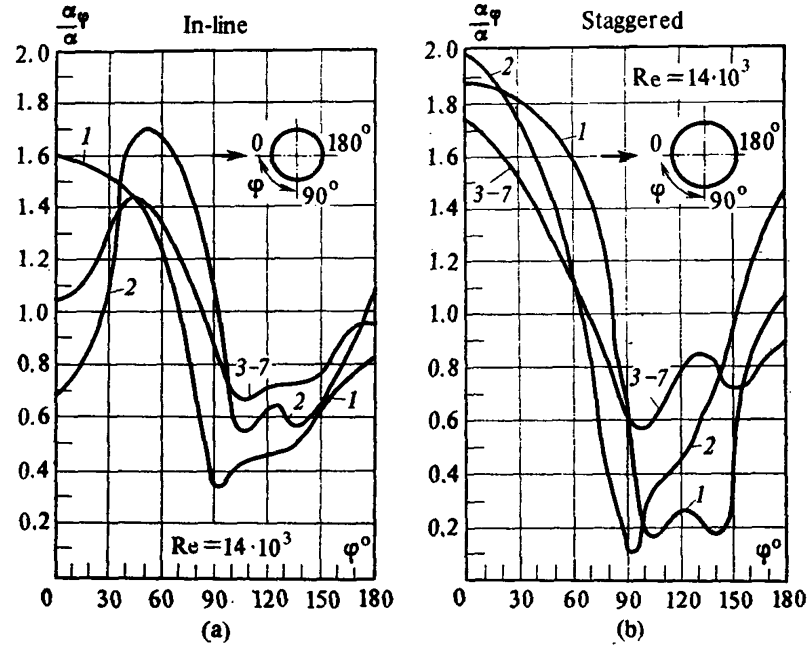


FIG. 27-8

the x-axis. Here $\bar{\alpha}$ is the circumferential mean heat-transfer coefficient for different rows, and α_φ is its local value.

It follows from the curves that for any row of tubes of a staggered bank the heat-transfer coefficient is maximum at the front part (when $\varphi=0$) and its variation differs but little from the variation of the heat-transfer coefficient of a single tube placed in cross fluid flow. The heat-transfer coefficient varies in the same manner for the first row of an in-line bank of tubes.

For tubes of the second and subsequent rows of an in-line bank of tubes there are two points at which the heat transfer coefficient is maximum at angles α_φ of about 50-60° to the direction of flow. From the foregoing it follows that the rate of heat transfer in the front as well as in the rear parts of the tubes will be lesser than the intensity of heat transfer for a single tube. With banks of tubes of either arrangement each row of tubes causes an additional turbulence in the fluid flow. Hence the heat transfer coefficient in the second row of tubes is greater than that in the first row, and the heat-transfer coefficient in the third row of tubes exceeds that in the second row. From the third row on, fluid flow stabilizes and the coefficient of heat transfer in all subsequent rows of tubes becomes constant.

Assuming the amount of heat transferred in the third row of a bank to be 100 per cent, the amount of heat transferred in the first row of either an in-line or a staggered bank of tubes is only 60 per cent. The heat trans-

ferred in the second row of an in-line bank amounts to 90 per cent, and for a staggered bank—to 70 per cent. As a whole the intensity of heat transfer in staggered banks is higher than in in-line banks due to better turbulization of flow in the former. In addition, heat transfer in banks of tubes depends on the spacing of the tubes, or the distance between them. This relationship is allowed for by a correction factor ε_s for the influence of the relative pitches.

For the deeper rows of an in-line bank of tubes

$$\varepsilon_s=\left(\frac{s_2}{d}\right)^{-0.15},$$

and of a staggered bank of tubes:

for $\frac{s_1}{s_2}<2\varepsilon_s=\left(\frac{s_1}{s_2}\right)^{0.166}$,

for $\frac{s_1}{s_2}\geqslant 2\varepsilon_s=1.12$.

In designing heat exchangers the mean heat-transfer coefficient for the third row of a bank of tubes exposed to fluid in the mixed pattern of flow ($\mathrm{Re}_{fd}\approx 1\times 10^3$ to 1×10^5) is calculated with the aid of the following formulae obtained by V. P. Isachenko:

for in-line banks of tubes

$$\overline{\mathrm{Nu}}_{fd}=0.26\ \mathrm{Re}_{fd}^{0.65}\ \mathrm{Pr}_f^{0.33}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}\varepsilon_s; \tag{27-19}$$

for staggered banks of tubes

$$\overline{\mathrm{Nu}}_{fd}=0.41\ \mathrm{Re}_{fd}^{0.6}\ \mathrm{Pr}_f^{0.33}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}\varepsilon_s. \tag{27-20}$$

When applied to air formulae (27-19) and (27-20) reduce to:

for in-line banks of tubes

$$\overline{\mathrm{Nu}}_{fd}=0.194\ \mathrm{Re}_{fd}^{0.65};$$

for staggered banks of tubes

$$\overline{\mathrm{Nu}}_{fd}=0.35\ \mathrm{Re}_{fd}^{0.6}.$$

When calculating the dimensionless terms we take the mean temperature of the fluid as the reference temperature—the velocity of fluid in the narrowest section of a row of tubes as the reference velocity, and the tube diameter as the reference dimension. The above formulae are valid for any liquids or gases.

The heat-transfer coefficient for the tubes of the first row is determined by multiplying the heat-transfer coefficient calculated for the third row by the correction factor $\varepsilon_1=0.6$; for tubes of the second row of staggered banks of tubes by $\varepsilon_2=0.7$ and by $\varepsilon_2=0.9$ in in-line banks of tubes.

The mean heat-transfer coefficient for a bank of tubes as a whole is determined by the averaging formula

$$\bar{\alpha}=\frac{\bar{\alpha}_1F_1+\bar{\alpha}_2F_2+\ldots+\bar{\alpha}_nF_n}{F_1+F_2+\ldots+F_n}, \tag{27-21}$$

where $\bar{\alpha}_1, \bar{\alpha}_2, \ldots, \bar{\alpha}_n$ = mean heat-transfer coefficients for individual rows of tubes;

$F_1, F_2, \ldots, F_n$ = heating surfaces of each row of tubes.

TABLE 27-4

Values of Correction Factor ε_ψ for Banks of Round Tubes

ψ	90	80	70	60	50	40	30	20	10
ε_ψ	1.0	1.0	0.98	0.94	0.88	0.78	0.67	0.52	0.42

If a bank of tubes is exposed to forced fluid flow directed at an angle $\psi<90°$, then the heat-transfer coefficient for a bank of tubes for which the angle $\psi=90°$ must be multiplied by a correction factor ε_ψ, taken from Table 27-4, $\bar{\alpha}_\psi=\varepsilon_\psi\bar{\alpha}_{90}$.

27-8. Heat Transfer in Liquid Metals

Sometimes, molten metals are used as working media. These have considerable merits. They have high boiling points, large heat-transfer coefficients and high thermal stabilities. Liquid metals are used in applications where it is necessary to transfer heat of high potentials at low pressures. Steam is of little use in these conditions: at high temperatures steam is at high pressure. Gases also possess essential disadvantage. They have low heat-transfer coefficients and small heat capacities. Sodium, potassium, sodium-potassium alloys, lithium, mercury, tin, bismuth and tin alloys are used as heat-carrying agents.

For alkaline and heavy metals in forced turbulent flow the heat-transfer coefficient can be determined by means of the following formula:

$$\overline{\mathrm{Nu}}_{fd}=4.8+0.014(\mathrm{Re}_{fd}\,\mathrm{Pr}_{fd})^{0.8}. \tag{27-22}$$

Here the reference temperature is the mean temperature of the liquid metal and the reference dimension is the equivalent diameter of the conduit. The formula is applicable when

$$\mathrm{Re}_{fd}=10^4-10^6, \quad \mathrm{Pr}_{fd}=0.004-0.032 \quad \text{and} \quad \frac{l}{d}>30.$$

When $l/d<30$ the correction for the length of the tube, ε_l, is determined from equation $\varepsilon_l=1.72(d/l)^{0.16}$. The coefficient of heat transfer in molten metals does not depend on the direction of heat flow or the temperature

difference. Formula (27-22) is applicable for clean heating surfaces and air-tight heating circuits filled with a neutral gas.

For free-convection heat transfer in alkaline and heavy metals and also in their alloys the following equation is recommended:

$$\overline{\mathrm{Nu}}_{fr\,h}=C\,\mathrm{Gr}_{Ah}^{n}\,\mathrm{Pr}_{fr\,h}^{0.4}. \qquad (27\text{-}23)$$

The quantities C and n in Eq. (27-23) depend on the $\mathrm{Gr}_{fr\,h}$ number when $\mathrm{Gr}_{fr\,h}=10^2\text{-}10^9$, $C=0.52$ and $n=0.25$ (laminar flow); when $\mathrm{Gr}_{fr\,h}=10^9\text{-}10^{13}$, $C=0.106$ and $n=0.33$ (turbulent flow). Here the reference temperature is the mean temperature of the boundary layer, $t_{bl}=\frac{t_f+t_w}{2}$.

Taken as the reference dimension are: for vertical plates—the height, for horizontal tubes—the outside diameter.

27-9. Heat Transfer in Gases at High Velocities

With the development of construction and calculation methods in the design of gas turbines, supersonic aircrafts, all kinds of rockets and other apparatus, the study of heat transfer in gases at supercritical velocities has acquired great practical importance.

Until recently the theory of convective heat transfer dealt with and studied processes where the working media moved at low velocities and the kinetic energy of flow did not cause a variation in fluid temperature. The change from low flow velocities to high came with the essential change in the conditions of heat transfer (for instance, in aircraft design). So, the equations of heat transfer given above cannot be applied without corresponding changes.

The mathematical statement, or equation, of the first law of thermodynamics for a flow, $dQ=di+\frac{dw^2}{2}$, establishes that for a working medium flowing through nozzles the associated external heat is expended to change its enthalpy and external kinetic energy. Under adiabatic conditions ($dQ=0$) the velocity of a gas flowing through nozzles increases and its temperature decreases. In diffusers the velocity of a working medium decreases and its temperature rises. Consequently, for adiabatic flow a decrease of the velocity of the working medium is accompanied by an increase of its temperature. A maximum rise in temperature is observed when there is stagnant flow, i.e. at a flow velocity equal to zero.

The stagnation temperature of an ideal gas in adiabatic flow, T_{st}, is determined from Eq. (13-5)

$$(i_2-i_1)+\frac{w_2^2-w_1^2}{2}=0,$$

or, assuming $c_p=\text{const}$,

$$c_p(T_2-T_1)+\frac{w_2^2-w_1^2}{2}=0.$$

If we relate T_2 and w_2 to the flow with zero velocity, (gas completely stagnant) and T_1 and w_1 to the cross section of flow that has not yet stagnated, we obtain

$$c_p T_2 = c_p T_1 + \frac{w_1^2}{2} \quad \text{or} \quad T_{st} = T_2 = T_1 + \frac{w^2}{2} c_p. \tag{27-24}$$

But for an ideal gas $c_p = \frac{k}{k-1} R$, therefore the stagnation temperature T_{st} of an ideal gas is equal to

$$T_{st} = T + \frac{k-1}{kR} \cdot \frac{w^2}{2} = T\left\{1 + \left(\frac{k-1}{2}\right)\left(\frac{w^2}{kTR}\right)\right\}, \tag{27-25}$$

where T is the thermodynamic temperature.

The velocity of sound propagation in an ideal gas is determined by equation $a = \sqrt{kvp} = \sqrt{kRT}$ or $a^2 = kRT$ using this Eq. (27-24) becomes

$$\frac{T_{st}}{T} = 1 + \frac{k-1}{2} \cdot \frac{w^2}{a^2} = 1 + \frac{k-1}{2} M^2, \tag{27-26}$$

where the ratio $\frac{w}{a}$ is denoted by M and referred to as the *Mach number*, which represents the ratio of flow velocity to the velocity of sound propagation in the flow. In the general case the quantity M can vary from zero to infinity. When $M < 1$ (gas flows at low velocities) the velocity of flow is lower than the velocity of sound; when $M = 1$ the velocity of flow is equal to the velocity of sound; when $M > 1$ the velocity of flow is higher than the velocity of sound. The Mach number permits determination of the effect of the kinetic energy of fluid flow on heat transfer.

When a gas flows past the surface of some body, due to the presence of internal friction forces, stagnation of the flow takes place, causing a rise of body temperature. The temperature of an adiabatically isolated body placed in the flow of a gas is called the *adiabatic*, or *equilibrium*, temperature. The adiabatic, or proper, temperature can be determined with the aid of a heat-insulated thermometer kept stationary in the flow of fluid. The thermodynamic temperature can be determined by means of a thermometer that is moving with the fluid. The difference between the adiabatic and the thermodynamic temperature is equal to

$$T_{ad} - T = r \frac{w^2}{2c_p} \quad \text{or} \quad T_{ad} = T + r \frac{w^2}{2c_p}, \tag{27-27}$$

where r is the *recovery factor* determining the fraction of kinetic energy converted into heat. The recovery factor depends on the physical properties of the flow, pattern of flow, the geometry of the body placed in the flow, etc. It is determined by comparing Eqs. (27-24) and (27-27)

$$r = \frac{T_{ad} - T}{T_{st} - T}.$$

With air in laminar flow at a plate $r = \sqrt{\mathrm{Pr}}$, while for turbulent flow $r = \sqrt[3]{\mathrm{Pr}}$, where Pr is the Prandtl number.

For other cases r is determined experimentally.

With a gas in high-velocity flow Newton's equation, $q=\alpha(T_f-T_w)$, cannot be applied. With gases at high velocities heat transfer must be calculated by equation

$$q=\alpha\left(T+r\frac{w^2}{2c_p}-T_w\right)=\alpha(T_{ad}-T_w). \tag{27-28}$$

At low velocities the quantity $r\frac{w^2}{2c_p}$ may be ignored and Eq. (27-28) reduces to Newton's equation. At $r=1$ the equation of heat transfer takes the form

$$q=\alpha(T_{st}-T_w). \tag{27-29}$$

For a plate placed in a longitudinal flow, when $M<1$, it is advisable to determine the mean heat-transfer coefficient by means of Eqs. (27-11) and (27-13). For a gas in flow in a tube when $M<1$, the mean heat-transfer coefficient can be determined by Eq. (27-9). At $M>1$ the recommended equations yield a value for the heat-transfer coefficient somewhat too high compared with the actual value.

27-10. Heat Transfer by Free Convection

Heat transfer by free convection arises because of the change in fluid density upon heating. Free convection takes place at the heated walls of furnaces and pipelines, in central-heating radiators, in refrigerators as food products are being chilled and so on. This mode of heat transfer is very important both for industry and for everyday life. Free convection takes place in a non-uniformly heated fluid, gas or liquid, occupying either a finite or an infinite space. If a body is at a temperature higher than that of the surrounding medium, then layers of the fluid are heated by the body. They become lighter and move upwards, acted upon by buoyancy forces, and are in turn replaced by colder layers coming from the surrounding space. So free convection comes about.

Deep and extensive experimental studies in heat transfer by free, or natural, convection have been carried out by academicians M. V. Kirpichev and M. A. Mikheyev and their colleagues.

Let us consider heat-transfer by free convection in an infinite space at a vertical plate or tube.

The free motion of the fluid arising at the vertical surfaces may be both laminar and turbulent. The pattern of fluid flow depends mainly on the temperature difference $\Delta t=t_w-t_f$, where t_w is the temperature of the heated surface and t_f is the temperature of the bulk of the fluid at a distance from the surface. With small temperature differences the fluid is in laminar flow along the entire surface. For large temperature differences the turbulent pattern of flow prevails. The shape of the body is of secondary importance for the development of free convection. Of primary importance for free convection is the length of the surface along which heat transfer takes place.

Problems in heat transfer by free convection with fluid in laminar and turbulent flow are solved analytically, making a number of simplifying assumptions. Because of these simplifications these solutions have not been widely used in practice. Our knowledge concerning the determination of the heat-transfer coefficient is based mainly on experiment.

Numerous investigations of heat transfer by free convection have been conducted with horizontal and vertical wires, tubes, plates and spheres. The experiments were conducted using air, hydrogen, carbon dioxide, water, oil and various organic liquids. These experimental results made it possible to obtain empirical criterion equations of similarity.

The mean coefficients of heat transfer by convection for fluid in free laminar flow along vertical walls can be determined with the aid of the following equations:

at $t_w = \text{const}$

$$\overline{\text{Nu}}_l = 0.63(\text{Gr}_l \text{Pr})^{0.25}; \tag{27-30}$$

at $q_w = \text{const}$

$$\overline{\text{Nu}}_{fl} = 0.75(\text{Gr}_{fl} \text{Pr}_f)^{0.25} \left(\frac{\text{Pr}_f}{\text{Pr}_w}\right)^{0.25}. \tag{27-31}$$

In these formulae, the temperature of the fluid at a distance from the wall is taken as reference, and the reference dimension is the length of the surface measured from the spot where heat transfer initiates. The formulae were derived for heat-carrying agents with a Prandtl number ranging from 0.7 to 3×10^3 and they should be applied when $10^3 < \text{Gr}_{fl} \text{Pr}_f < 10^9$.

For fluid in free turbulent motion along a vertical wall, where $\text{Gr}_{fl} \text{Pr}_f > 6 \times 10^{10}$ the mean heat-transfer coefficients can be calculated from the following formula*

$$\text{Nu}_{fl} = 0.15(\text{Gr}_{fl} \text{Pr}_f)^{0.33} \left(\frac{\text{Pr}_f}{\text{Pr}_w}\right)^{0.25}. \tag{27-32}$$

The reference temperature and linear dimension are the same as in formula (27-31).

If $10^9 < \text{Gr}_{fl} \cdot \text{Pr}_f < 6 \times 10^{10}$, then the fluid is in the free transition pattern of flow along the vertical wall. The pattern of transition flow is characterized by the instability of both flow and the process of heat transfer. A typical illustration of free flow of fluid and the variation of the heat-transfer coefficient along a vertical wall is given in Fig. 27-9.

At the lower section of the wall the rising air (fluid) with a low velocity is observed to be in laminar flow with a laminar boundary layer gradually increasing in thickness. At some distance from the bottom end of the wall deterioration of the laminar boundary layer initiates, and wave motion of the fluid starts that changes gradually into a developed turbulent flow with

* Formule (27-31) and (27-32) were derived by I. M. Pchelkin.

a laminar sublayer in direct proximity to the tube surface. The heat-transfer coefficient varies in accordance with the change of the thickness of the boundary layer and of the pattern of fluid flow at the surface of the tube. As the thickness of the laminar boundary layer increases, the heat-transfer coefficient decreases from the bottom of the wall upwards. The heat-transfer coefficient is minimum at the spot where the laminar boundary layer has maximum thickness. In the region where there is wave flow, the heat-transfer coefficient gradually increases and assumes a maximum constant value in the region of developed turbulent fluid flow. In Fig. 27-9 the heat-transfer coefficient α is plotted as a function of wall height only. The change in the physical properties of the fluid and the temperature difference with height may cause a change in the heat-transfer coefficients. On the average under the transition pattern of flow, the rate of heat transfer increases from the magnitude corresponding to laminar flow to a value characteristic of turbulent fluid flow. The greatest and smallest values of the heat-transfer coefficient for fluid in transition flow can be determined respectively by formulae (27-32) and (27-31).

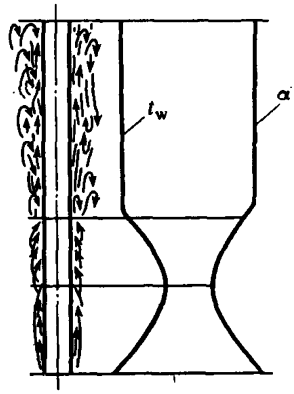


FIG. 27-9

The pattern of free-convection flow near hot horizontal tubes of different diameters is illustrated in Fig. 27-10. With tubes of small diameter the rising fluid remains in laminar flow even at a distance from the tube. With tubes of larger diameter the change from laminar to turbulent flow may occur even within the limits of the tube surface itself.

Mean coefficients of heat transfer in fluid in free laminar flow near horizontal tubes may be calculated from the formula suggested by I. M. Mikheyeva

$$\overline{\mathrm{Nu}}_{fl}=0.5(\mathrm{Gr}_{fd}\,\mathrm{Pr})^{0.25}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}. \qquad (27\text{-}33)$$

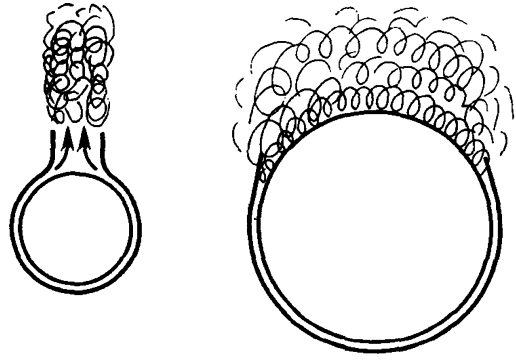


FIG. 27-10

In formula (27-33) the reference temperature is that of the liquid or gas at a distance from the tube, and the reference linear dimension is the tube diameter.

Free convection near horizontal hot surfaces is of a special character and the pattern of fluid flow depends on the position and size of plates (this is treated in detail in specialized literature). However, the heat-transfer coefficient for horizontal surfaces can be calculated approximately by formula (27-33). When the hot surface faces upward, the heat-transfer coefficient calculated using formula (27-33) must be increased by 30 per cent. When the hot surface faces downward, the heat-transfer coefficient should be decreased by 30 per cent. In these cases the smaller side of the plate is taken as the reference dimension.

Heat transfer by free convection in a finite space is a more intricate process governed by other quantitative laws. Approximate calculations for the most important application can be found in special literature devoted to the subject.

Typical Questions and Examples to Chapter Twenty Seven

1. What is meant by mean fluid temperature?
2. How is the mean fluid temperature determined?
3. How is the mean velocity of fluid determined?
4. How is the equivalent diameter of conduits of non-circular cross section determined?
5. Up to what Reynolds number is the fluid flow unable to change from the laminar pattern to the turbulent pattern?
6. How does free convection affect heat transfer in fluid in laminar flow?
7. What criterion equations are recommended for fluids in laminar flow?
8. What criterion equations are recommended for fluids in turbulent flow?
9. What are the distinguishing features of heat transfer in coils?
10. What criterion equations are recommended to calculate heat transfer in a fluid in free flow along a plate?
11. What are the distinguishing features of heat transfer by convection for a single tube in cross flow?
12. What criterion equations are recommended to calculate the heat transferred by free convection for a single tube in cross flow?
13. What kind of tube banks find application in engineering?
14. Describe in detail the pattern of fluid flow past banks of tubes placed in cross flow.
15. What criterion equations are recommended to calculate heat transfer in banks of tubes in cross flow?
16. How is the mean heat-transfer coefficient for a bank of tubes determined?
17. What are the peculiar features of heat transfer in liquid metals?

18. What criterion equations may be used to calculate heat transfer in liquid metals?
19. State the peculiar features of heat transfer in fluids at high velocities.
20. What is meant by stagnation temperature?
21. What is characterized by the Mach number?
22. What is meant by adiabatic temperature?
23. What is meant by the recovery factor?
24. What criterion equations are used to calculate heat transfer in fluids at high velocities?
25. Describe the mechanism of the appearance of free convection.
26. Describe the peculiarities of free-convection fluid flow near a vertical wall.
27. What criterion equations are used to calculate heat transfer in fluids in free flow?

Example 27-1. Determine the heat-transfer coefficient and the quantity of heat transferred as water flows in a horizontal tube having a diameter $d=0.008$ m and length $l=6$ m, assuming a velocity $w=0.1$ m/s and a water temperature $t_f=80$ °C; tube wall temperature $t_w=20$ °C.

At $t_f=80$ °C, $\lambda_f=0.675$ W/m·deg, $\nu_f=0.365\times10^{-6}$ m²/s, $\beta_f=6.32\times10^{-4}$ 1/deg, $\mathrm{Pr}_f=2.21$.

At $T_w=293$ K $\mathrm{Pr}_w=7.02$.

With these values of the quantities we obtain

$$\mathrm{Re}_{fd}=\frac{wd}{\nu}=\frac{0.1\times0.008\times10^6}{0.365}=2190;$$

$$\mathrm{Re}_{fd}^{0.33}=13.2; \quad \mathrm{Pr}_f^{0.43}=1.4; \quad \left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}=0.75.$$

The temperature difference $t_f-t_w=60$ °C. The Grashof number

$$\mathrm{Gr}_{fd}=\frac{gd^3\beta\,\Delta T}{\nu^2}=\frac{9.81\times0.008^3\times6.32\times10^{-4}\times60}{(0.365\times10^{-6})^2}=1.43\times10^6; \quad \mathrm{Gr}_{fd}^{0.1}=4.12.$$

Using formula (27-6), we find

$$\overline{\mathrm{Nu}}_{fd}=0.15\,\mathrm{Re}_{fd}^{0.33}\,\mathrm{Pr}_f^{0.43}\,\mathrm{Gr}_{fd}^{0.1}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25};$$

$$\overline{\mathrm{Nu}}=0.15\times13.2\times1.4\times4.12\times0.75=8.56,$$

whence

$$\alpha=\overline{\mathrm{Nu}}_{fd}\frac{\lambda_f}{d}=\frac{8.56\times0.675}{0.008}=724 \text{ W/m}^2\cdot\text{deg}.$$

The correction for the length of the tube should not be introduced since the ratio $\frac{l}{d}>50$.

The quantity of heat transferred through the entire tube

$$Q=\pi dl\alpha(t_f-t_w)=3.14\times0.008\times6\times724\times60=6540 \text{ W}.$$

Example 27-2. Determine the coefficient of heat transfer α from air flowing with a velocity $w=10$ m/s to the wall of a straight tube having a diameter $d=0.1$ m and length $l=2$ m. The mean temperature of the air $t_f=120$ °C.

With $t_f=120$ °C $\lambda_f=0.0334$ W/m·deg;

$\lambda_f=25.45\times10^{-6}$ m²/s.

Under these conditions

$$\mathrm{Re}_{fd}=\frac{wd}{\nu}=\frac{10\times0.1\times10^6}{25.45}=39\,200;$$

$$\mathrm{Re}_{fd}^{0.8}=4730.$$

Substituting the values of these quantities into Eq. (27-9), we obtain

$$\mathrm{Nu}_{fd}=0.018\,\mathrm{Re}_{fd}^{0.8}=0.018\times4730=85.2,$$

whence

$$\alpha=\mathrm{Nu}_{fd}\frac{\lambda_f}{d}=\frac{85.2\times0.0334}{0.1}=28.4\ \mathrm{W/m^2\cdot deg}.$$

Since $\frac{l}{d}=\frac{2}{0.1}=20<50$, it is necessary to introduce the correction factor ε_l, taken from Table 27-1 and equal to 1.13. Then the heat-transfer coefficient α_r is equal to

$$\alpha_r=\alpha\varepsilon_l=28.4\times1.13=32.2\ \mathrm{W/m^2\cdot deg}.$$

Example 27-3. A flat plate, 1.5 m wide and 2.0 m long (l), is exposed to longitudinal air flow at a temperature $T_f=293$ K with velocity $w=4.0$ m/s. Calculate the heat-transfer coefficient α and the heat flux Q, if the surface temperature of the plate $T_w=353$ °K.

At $T_f=293$ K $\lambda_f=0.0223$ W/m·deg; $\nu_f=15.06\times10^{-6}$ m²/s.

With these quantities

$$\mathrm{Re}_{fl}=\frac{wl}{\nu}=\frac{4\times0.2\times10^6}{15.06}=532\,000;$$

$$\mathrm{Re}_{fl}^{0.8}=38\,000.$$

Substituting the values obtained into formula (27-14), we find

$$\mathrm{Nu}_{fl}=0.032\,\mathrm{Re}_{fl}^{0.8}=0.032\times38\,000=1216.0,$$

whence

$$\alpha=\mathrm{Nu}_{fl}\frac{\lambda_f}{l}=\frac{1216\times0.0223}{2}=13.5\ \mathrm{W/m^2\cdot deg}.$$

The quantity of heat transferred from the plate to the air,

$$Q=\alpha F\,\Delta T=13.5\times3\times60=2430\ \mathrm{W}.$$

Example 27-4. A cylindrical tube having an outside diameter $d=30$ mm and length $l=5$ m is cooled with water in cross flow at a temperature $T_f=283$ K. Water velocity $w=2$ m/s. The tube surface temperature $T_w=353$ K and the angle of attack is 50°.

Determine the coefficient of heat transfer from the surface of the tube to the cooling water and the amount of heat transferred.

At the water temperature $T_f=283$ K $\lambda_f=0.575$ W/m·deg and $\nu_f=1.306\times10^{-6}$ m²/s.

Under these conditions

$$\mathrm{Re}_{fd}=\frac{wd}{\nu}=\frac{2\times0.03\times10^6}{1.306}=46\,000;$$

$$\mathrm{Re}_{fd}^{0.6}=630; \quad \mathrm{Pr}_f=9.52; \quad \mathrm{Pr}_f^{0.38}=2.35;$$

$$\mathrm{Pr}_w=2.21; \quad \left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}=\left(\frac{9.52}{2.21}\right)^{0.25}=1.44.$$

Substituting these values into formula (27-16), we obtain

$$\mathrm{Nu}_{fd}=0.25\,\mathrm{Re}_{fd}^{0.6}\,\mathrm{Pr}_f^{0.38}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}=0.25\times630\times2.35\times1.44=534,$$

whence

$$\alpha=\mathrm{Nu}_{fd}\frac{\lambda_f}{d}=\frac{534\times0.575}{0.03}=10\,200 \text{ W/m}^2\cdot\text{deg}.$$

Allowing for the angle of attack, we find from Table 27-3 the correction factor $\varepsilon_\varphi=0.87$, consequently,

$$\alpha_r=10\,200\times0.87=8880 \text{ W/m}^2\cdot\text{deg}.$$

The amount of heat transferred to the tube,

$$Q=\pi dl\alpha_r\,\Delta T=3.14\times0.03\times5\times8880\times70=292\,000 \text{ W}=292 \text{ kW}.$$

Example 27-5. Determine the mean coefficient of heat transfer by convection from a cross flow of flue gases consisting of $H_2O=11$ per cent, $CO_2=13$ per cent and $N=76$ per cent to the walls of an eight-row bank of tubes of staggered arrangement. The tube diameter is $d=60$ mm. The mean gas velocity in the narrowest cross section of the bank is $w=10$ m/s. The temperature of the flue gases at the inlet to the bank, $T_{f1}=1473$ K, and at the outlet from the bank, $T_{f2}=1073$ K. The angle of attack is 50°. Fouling of the tubes is to be ignored. The pressure of the steam carried by the tubes is 100 bar and tube surface temperature $T_w=584$ K. For the sake of comparison, also solve the problem for an in-line bank of tubes in cross flow under the same conditions.

With tubes in cross flow heat transfer is calculated for the third row of tubes by the following equations: for tubes arranged in-line—by formula (27-19)

$$\mathrm{Nu}_{fd}=0.26\,\mathrm{Re}_{fd}^{0.65}\,\mathrm{Pr}_f^{0.33}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25};$$

for tubes in staggered arrangement—by formula (27-20)

$$\mathrm{Nu}_{fd}=0.41\,\mathrm{Re}_{fd}^{0.6}\,\mathrm{Pr}_f^{0.33}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}.$$

The reference dimension here is the tube diameter and the reference temperature is the average fluid temperature

$$T_f=0.5(T_{f1}+T_{f2})=1273\ \mathrm{K}.$$

At $T_f=1273$ K the values of the physical properties are as follows: $\nu_f=174.3\times10^{-6}$ m²/s; $\lambda_f=0.109$ W/m·deg; $\mathrm{Pr}_f=0.58$; $\mathrm{Pr}_w=0.652$; $\mathrm{Pr}_f^{0.33}=0.58^{0.33}=0.835$;

$$\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}=0.892^{0.25}=0.97.$$

Under these conditions

$$\mathrm{Re}_{fd}=\frac{wd}{\nu}=\frac{10\times0.06\times10^6}{174.3}=3450;$$

$$\mathrm{Re}_{fd}^{0.65}=200;\qquad \mathrm{Re}_{fd}^{0.6}=3450^{0.6}=133.$$

For tubes in in-line arrangement let us substitute the values of all quantities into Eq. (27-19)

$$\mathrm{Nu}_{in}=0.26\times200\times0.835\times0.97=42.1;$$

for tubes in staggered arrangement—into Eq. (27-20)

$$\mathrm{Nu}_{st}=0.41\times133\times0.835\times0.97=44.2.$$

The coefficient of heat transfer in the third row of the in-line bank of tubes

$$\alpha_{in\,3}=\mathrm{Nu}_{in}\frac{\alpha_f}{d}=\frac{42.1\times0.109}{0.06}=76.7\ \mathrm{W/m^2\cdot deg};$$

for the staggered bank of tubes

$$\alpha_{st\,3}=\mathrm{Nu}_{st}\frac{\lambda_f}{d}=\frac{44.2\times0.109}{0.06}=80.3\ \mathrm{W/m^2\cdot deg}.$$

The coefficient of heat transfer in the first row of the two banks of tubes is as follows:

$$\alpha_{in\,1}=0.6\,\alpha_{in\,3}=76.7\times0.6=46.0\ \mathrm{W/m^2\cdot deg};$$

$$\alpha_{st\,1}=0.6\,\alpha_{st\,3}=80.3\times0.6=48.2\ \mathrm{W/m^2\cdot deg}.$$

For tubes of the second row of the banks:

$$\alpha_{in\,2}=0.9\,\alpha_{in\,3}=0.9\times76.7=69.0\ \mathrm{W/m^2\cdot deg};$$

$$\alpha_{st\,2}=0.7\,\alpha_{st\,3}=0.7\times80.3=56.2\ \mathrm{W/m^2\cdot deg}.$$

With the same surface of the rows of tubes, the mean heat-transfer coefficient is equal to:

for an in-line bank of tubes

$$\bar{\alpha}_{in}=\frac{46.0+69.0+6\times76.7}{8}=71.9 \text{ W/m}^2\cdot\text{deg};$$

for a staggered bank of tubes

$$\bar{\alpha}_{st}=\frac{48.2+56.2+6\times80.3}{8}=73.4 \text{ W/m}^2\cdot\text{deg}.$$

Allowing for an angle of attack $\psi=50°$, we find from Table 27-4 a correction factor $\varepsilon_{\psi}=0.88$. Then, the mean heat-transfer coefficient for the in-line bank of tubes will be equal to $\bar{\alpha}_{in}=71.9\times0.88=63.27$ W/m²·deg; for the staggered bank of tubes $\bar{\alpha}_{st}=73.4\times0.88=64.59$ W/m²·deg.

Under the same conditions of flow the rate of heat transfer in staggered banks of tubes exceeds that in in-line banks by about 3 per cent in the given problem.

Example 27-6. Determine the intensity of heat transfer by free convection from a vertical bare, non-insulated, pipeline having a diameter $d=120$ mm and a height (length) $h=6$ m to air. Tube wall temperature $T_w=523$ K, air temperature $T_f=293$ K.

The physical quantities are taken at an ambient temperature $T_f=293$ K

$$\lambda_f=0.026 \text{ W/m}\cdot\text{deg}; \quad \text{Pr}_{fd}=0.703; \quad \frac{\text{Pr}_f}{\text{Pr}_w}=1;$$

$$\nu_f=15.06\times10^{-6} \text{ m}^2/\text{s}.$$

The Grashof number

$$\text{Gr}_{fd}=\frac{\beta h^3 g\,\Delta T}{\nu^2}=\frac{6^3\times9.81\times230\times10^{12}}{293\times15.06^2}=7.34\times10^{12};$$

$$\text{Gr}_{fd}\,\text{Pr}_{fd}=7.34\times10^{12}\times0.703=5.16\times10^{12}.$$

Under these conditions the air is in turbulent flow and the heat-transfer coefficient is determined from Eq. (27-32)

$$\text{Nu}_{fd}=0.15(\text{Gr Pr})_{fd}^{0.33}=0.15(5.16\times10^{12})^{0.33}=2320.$$

Whence the coefficient of heat transfer

$$\alpha=\frac{N_{fd}\lambda_f}{h}=\frac{2320\times0.026}{6}=10.0 \text{ W/m}^2\cdot\text{deg}.$$

The amount of heat lost from the bare pipeline to the surroundings

$$Q=\alpha F(T_w-T_f)=10\times3.14\times0.12\times6\times230=5200 \text{ W}.$$

CHAPTER TWENTY EIGHT

HEAT TRANSFER IN BOILING LIQUIDS AND CONDENSING VAPOURS

28-1. Heat Transfer in Boiling Liquids

Until now we have been studying processes in which the working medium does not change its state of aggregation (no changes of phase take place). This chapter will be devoted to the processes of the boiling of a liquid, where there is a change from the liquid to the vapour phase, and the condensation of a vapour, where there is a change from the vapour to the liquid phase.

Let us consider the process of heat transfer in a boiling liquid.

The *boiling* of a liquid is defined as the process of vaporization characterized by the appearance of new interfaces between the liquid and vapour phases inside the liquid, when it is heated to a temperature above the saturation temperature.

The characteristic feature of the boiling is the formation of vapour bubbles. Two kinds of boiling are distinguished: boiling on a solid heat-transfer surface (local boiling), and boiling in the whole volume of a liquid (bulk boiling).

Boiling on a solid heat-transfer surface may arise when the temperature of the liquid is higher than its saturation temperature at the same pressure, and the temperature of the heat-transfer surface is greater than the temperature of the boiling liquid. Vapour bubbles form directly on the heat-transfer surface.

Bulk boiling takes place when the liquid is superheated relative to the saturation temperature at the given pressure. Bulk boiling can be induced by a rapid decrease of pressure or when there are inner heat sources in the liquid.

In modern power engineering boiling processes on solid heating surfaces are common, so this kind of boiling will be considered below.

From the heating surface, having a temperature t_w exceeding the saturation temperature t_s, heat is transferred to the boundary layer of the liquid and from this layer to the bulk of the liquid and the forming vapour. One side of the boundary layer is at wall temperature and the temperature of the other side of the layer is equal to the temperature of the boiling liquid, i.e. in the boundary layer the liquid is superheated relative to the bulk of liquid temperature by $\Delta t = t_w - t_f$. The temperature difference Δt increases with an increase of the density of heat flow q. With $q = 22\,220$ W/m^2 and a temperature of saturated vapour, $t_s = 100$ °C, the temperature of the

bulk of the liquid is equal to 100.4 °C and the temperature of the boundary layer is equal to 109.1 °C.

Observations have shown that vapour bubbles originate only on the heat-transfer surface in the superheated boundary layer of liquid and only at individual points of this surface, referred to as *starting points of vaporization*. The starting points for vapour bubbles may be surface irregularities on the heat-transfer wall, particles of scale or bubbles of gas evolving from the liquid. The number of forming vapour bubbles is larger, the more starting points there are, the higher is the superheating of the boundary layer, the greater is the temperature difference, or the larger is the rate of heat flow through the heat-transfer surface.

As the vapour bubbles grow to a definite size they separate from the surface and float upwards, and new bubbles form at the starting points of vaporization. The size of the forming vapour bubbles depends to a great extent on the wetting ability of the liquid. If the boiling liquid wets the heat-transfer surface properly, then the vapour bubbles have a thin root and separate easily (Fig. 28-1*a*). If the boiling liquid fails to wet the heat-transfer surface, the vapour bubble has a thick root, with the top part of

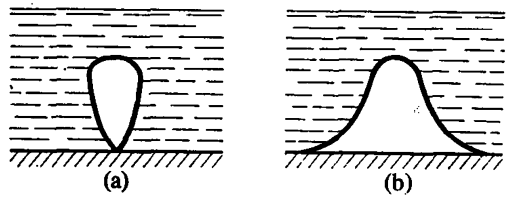


FIG. 28-1

the bubble separating from the surface and the root remaining on it (Fig. 28-1*b*).

The growth of bubbles to separation size and their motion after separation from the heat-transfer surface cause an intensive circulation and mixing of the liquid in the boundary layer, resulting in a sharp increase of the intensity of heat transfer from the surface to the liquid. This kind of boiling is referred to as *nucleate boiling*.

If the liquid is still underheated (at atmospheric pressure $\Delta t \leqslant 5$ °C), then the vapour bubbles forming on the surface proper condense immediately upon separation and boiling is restricted to a thin boundary layer of superheated liquid at the surface. The vapour bubbles then weakly mix the layer adjoining the wall and heat transfer takes place mainly by free convection. This kind, or regime, of boiling is referred to as *surface boiling*.

With nucleate boiling the surface of contact between the root of a vapour bubble and the heat-transfer surface is very small, so almost all the heat is transferred from the hot surface to the boundary layer of liquid and from the latter into the bulk of liquid by convection.

With an increase of the temperature difference or of the rate of heat flow the number of the starting points of vaporization increases continuously and, finally, there exist so many starting points that individual vapour bubbles merge, or coalesce, into a continuous vapour layer which bursts periodically at some spots, and the vapour forming breaks through into the bulk of boiling liquid. Boiling of this kind is referred to as *film boiling*.

Due to its low thermal conductivity the continuous vapour layer constitutes a great thermal resistance to heat flow [at $p=1$ bar, for water $\lambda_f \approx 0.68$, while for steam (water vapour) $\lambda_{st} \approx 0.02$ W/m·deg]. The rate of heat transfer from the wall to the liquid drops sharply and the temperature difference increases considerably. As this takes place the heat-transfer coefficient diminishes abruptly and if the rate of heat flow q remains the same, then, as is seen from the equation $q=\alpha(t_w-t_f)$, when the temperature of the liquid is constant wall temperature t_w must rise considerably, which may bring about burnout of the heat-transfer surface and damage to the apparatus.

Investigations have shown that for a liquid in bulk boiling under conditions of free motion the heat-transfer coefficient depends on the physical properties of the liquid, the temperature difference and the pressure. The shape of the vessel does not greatly affect the process of heat transfer.

In Fig. 28-2 the coefficient of heat transfer in boiling water and the rate of heat flow are plotted as a function of the temperature difference Δt.

With small temperature differences, up to 5 °C, the magnitude of the heat-transfer coefficient is determined by the conditions of free convection in a single-phase liquid (region *AB*). With an increase in Δt the heat-transfer coefficient increases rapidly and intensive nucleate boiling takes place. At point *K* there occurs a change in the kind, or mode, of boiling. Nucleate boiling turns into film boiling and with a further increase in Δt the heat-transfer coefficient decreases abruptly. This change from nucleate to film

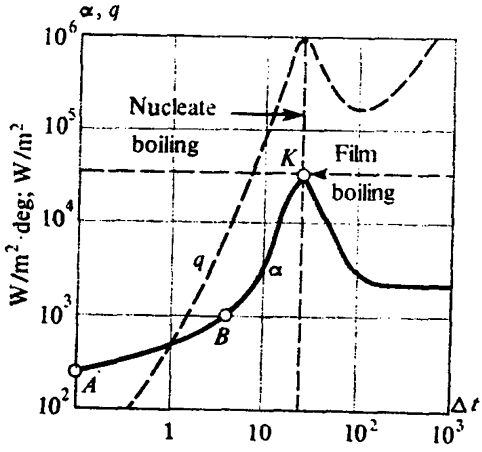


FIG. 28-2

boiling is accompanied by such an intensive formation of vapour bubbles that there is no time for them to separate and they form a continuous vapour film which isolates the liquid from the wall, and film boiling sets in.

The values of Δt, α and q at which nucleate boling turns into film boiling are referred to as *critical* or *peak values*. The establishment of the existence of a critical temperature difference Δt_{cr} is of great practical importance in choosing optimal operating conditions for boilers and evaporators.

By developing experimental data on the basis of the theory of similarity, G. N. Kruzhilin suggested determining the heat-transfer coefficient and the critical (or peak) flux for a liquid in the state of nucleate boiling under conditions of free convection in a large volume by means of the following generalized formulae:

$$\alpha = 0.008 \left(\frac{\varrho'' r}{\varrho' - \varrho''}\right)^{0.033} \left(\frac{\varrho'}{\sigma}\right) \frac{\lambda^{0.75} q^{0.7}}{\mu^{0.45} c^{0.12} T_s^{0.37}}; \tag{28-1}$$

$$q_{peak} = 5466 \frac{\lambda^{0.4} (\varrho' - \varrho'')^{0.48} (\varrho'' r)^{0.36} T_s^{0.32} \sigma^{0.21}}{\varrho'^{0.31} \mu^{0.14} c^{0.8}}, \tag{28-2}$$

where ϱ' and ϱ'' = densities of liquid and vapour; kg/m^3;
r = heat of vaporization, kJ/kg;
σ = surface tension, kg/m;
λ = thermal conductivity of liquid, W/m·deg;
μ = dynamic viscosity of liquid;
c = heat capacity of liquid, kJ/kg·deg;
T_s = absolute temperature of saturated vapour at the given pressure, deg.

Making use of the data proposed by G. N. Kruzhilin, Academician M. A. Mikheyev recommended using the very simple formulae for water in nucleate boiling for pressures ranging from 0.2 to 80 bar

$$\alpha = 3.15 p^{0.15} q^{0.7}; \quad \alpha = 46 \Delta t^{2.33} p^{0.5}. \tag{28-3}$$

Hence $\Delta t = t_w - t_s$ = temperature difference, deg;
p = absolute vapour pressure, bar;
q = rate of heat flow, W/m^2.

28-2. Heat Transfer in Condensing Vapours

The process of condensation takes place when under certain conditions a vapour changes both to either liquid or solid state. The process of condensation is often encountered in practice: in condensers of steam turbines; in desalination plants in which drinking water is produced from sea water; in the heat exchangers of refrigerating plants and machines, and so on.

Condensation of a vapour is always associated with heat transfer through the surface of condensation and simultaneous removal of the forming

substance—the condensate. Condensation is only possible when the temperature and pressure of a vapour are below the temperature and pressure at the critical point. Condensation proceeds both within the volume of a vapour and on solid cooled surfaces. Condensation on solid surfaces is most commonly encountered in practice.

When a saturated or superheated vapour is in contact with a wall whose temperature is below the saturation temperature at the given pressure, then, due to heat transfer, the vapour cools and condenses. The condensate forms on the surface as a film or as drops and flows down.

Depending on the state of the surface, two kinds of condensation are distinguished: *dropwise* and *film condensation.* If the condensing liquid fails to wet the surface (the surface may be coated with grease, kerosene, oil products, for instance), and the condensate forms on the surface in individual drops, dropwise condensation takes place. On the wetted surface of a steam-turbine condenser, the condensing saturated steam forms a continuous film of definite thickness. Condensation of this kind is referred to as film condensation.

For water vapour (steam) dropwise condensation is random, unstable and short lived. It is marked by an intensive heat transfer and the heat-transfer coefficient is 15 to 20 times greater than that associated with film condensation. This phenomenon is explained by the fact that the condensing vapour is in direct contact with the cooled surface.

At the present time extensive studies are being conducted with the aim of provoking artificial dropwise condensation with the aid of special substances, called *lyophobic agents* (*hydrophobic agents* in the case of steam condensation). These substances are introduced into the steam or are applied to the heat-transfer surface of a heat exchanger. To ensure stable dropwise condensation of steam, it is necessary to add the hydrophobic agents continuously, since they are continually washed off by the forming condensate or else they dissolve in it. Many organic compounds are used as hydrophobic agents, but they are short-lived.

In heat exchangers operating with pure water vapour film condensation is usually observed. In the top part of a vertical wall or tube the condensate film flows down with a low velocity and the flow of the film is laminar. As the velocity of the condensate rises the laminar flow of the film changes to turbulent flow.

With film condensation the heat of the condensing vapour is transferred to the surface of the condensate film and the film transfers the heat to the wall. The condensate film offers a considerable thermal resistance to heat flow and the thicker the film the smaller is the rate of heat flow.

Let us consider the process of heat transfer in the event of film condensation with the condensate film in laminar flow.

In the case considered heat is transported through the film only by conduction. Let the surface of the condensate film facing the vapour be at temperature t_s (the saturation temperature), and the surface of the condensate film in contact with the wall be at a temperature t_w. Then, if the thermal

conductivity of the condensate is λ and the condensate film thickness δ, the rate of heat flow is equal to

$$q=\frac{\lambda}{\delta}(t_s-t_w).$$

In addition, we know from Newton's law that if the heat-transfer coefficient is α, the rate of heat flow is equal to

$$q=\alpha(t_s-t_w),$$

whence

$$\alpha=\frac{\lambda}{\delta}. \tag{28-4}$$

It follows from Eq. (28-4) that the heat-transfer coefficient depends on the thickness of the condensate film flowing down the wall and the thicker this layer the smaller is the rate of heat transfer.

The theory of vapour condensation is based on the investigations conducted by Nusselt, who calculated the thickness of the condensate film, and then, integrating the quantity of heat passing through a vertical wall with a height H, found the equation for the heat-transfer coefficient.

However, in creating his theory of condensation Nusselt made a number of simplifying assumptions, so the derived equation may be considered only an approximation.

In addition to the investigations conducted by Nusselt, Academician P. L. Kapitsa has shown the film of condensate to be in wave flow on vertical surfaces. Using the results of theoretical studies, P. L. Kapitsa proved that for vapour condensing on a vertical wall the heat-transfer coefficient is 21 per cent greater than the coefficient for pure laminar flow described by the equation derived by Nusselt. So in practical calculations it is advisable to determine the mean heat-transfer coefficient by means of the following formulae:

for a vertical wall

$$\bar{\alpha}_{vert}=1.14\sqrt[4]{\frac{g\varrho_f r\lambda_f^3}{\nu_f H(t_s-t_w)}}; \tag{28-5}$$

for a horizontal wall

$$\bar{\alpha}_{hor}=0.72\sqrt[4]{\frac{g\varrho_f r\lambda_f^3}{\nu_f d(t_s-t_w)}}, \tag{28-6}$$

where g = gravitational acceleration;
λ_f = thermal conductivity of liquid;
r = heat of vaporization;
ϱ_f = density of liquid;
ν_f = kinematic viscosity of liquid;

H = height of vertical wall;
t_s = temperature of saturated vapour;
t_w = surface temperature of the wall;
d = outside tube diameter.

The physical properties of condensate, λ_f, ν_f and ϱ_f, are taken at the mean temperature of the condensate film, equal to $0.5(t_s+t_w)$. The heat of vaporization r is chosen at the saturation temperature t_s.

In the general form, for laminar flow, the equation of heat transfer in condensing vapour, expressed in terms of dimensionless groups, has the following form:

$$\mathrm{Nu}=C\sqrt{\mathrm{GaKPr}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)}, \tag{28-7}$$

where K is the phase-transition number, equal to

$$K=\frac{r}{c_{pf}\Delta t}$$

The above formula is valid for vapours of various substances.

The mass of condensate forming on 1 m^2 of surface is determined by the formula

$$m=\frac{q}{r}=\frac{\lambda}{\delta r}(t_s-t_w). \tag{28-8}$$

Condensate is measured in units of kg/s·m^2.

Since the height of a tube is always greater than its diameter, the coefficient of heat transfer for horizontal tubes is greater than that for vertical tubes.

28-3. The Effect of Various Factors on Heat Transfer in Condensing Vapours

Formulae (28-5) and (28-6) hold for stagnant or slowly moving vapour ($w<10$ m/s). If the direction of vapour flow coincides with that of the condensate film, the thickness of the latter decreases and the heat-transfer coefficient increases. If the vapour and condensate film move in opposite directions the thickness of the condensate film increases and the heat-transfer coefficient diminishes. However when vapour moves with a comparatively high velocity the condensate film is torn off the surface resulting in a considerable increase of the heat-transfer coefficient.

When superheated vapour undergoes condensation its temperature at the wall drops gradually and in fact it is saturated vapour that condenses. It follows from this that when superheated vapour condenses it transfers to the forming condensate the heat of vaporization and the superheating heat, $r'=r+c_{pm}(t-t_s)$, where c_{pm} is the mean heat capacity of the superheated vapour at a given pressure and t is the superheated vapour temperature. Hence for condensing superheated vapour the heat-transfer coefficient can

be calculated by the same formulae as for saturated vapour, but the heat of vaporization r must be replaced by the quantity r'. The temperature difference is taken as $\Delta t = t_s - t_w$ as above. This is because if $t_w < t_s$ then the vapour condenses in the condensate film and a temperature t_s sets in at the interface.

The state of the surface of a condenser is also of great importance. When vapour condenses on tubes covered with rust and the surfaces of the tubes are rough, the thickness of the condensate film increases, causing a decrease of the heat-transfer coefficient by more than 30 per cent, compared with a smooth clear surface.

The mixture of various gases in the vapour markedly reduce the rate of heat transfer upon condensation. This is because the vapour condenses and the gas or air is left on the cold tube as a layer through which vapour molecules can penetrate from the core of the flow only by diffusion. This greatly increases the thermal resistance of the condensate film. So, the presence of 1 per cent of air in vapour reduces the rate of heat transfer upon condensation by 60 per cent (moving vapour is less affected by the presence of air).

Of great importance for ensuring high heat-transfer coefficients upon condensation of vapour is the correct arrangement of the tubes of a condenser. Vertical tubes are usually fitted with caps, installed at 10-cm intervals, that draw off the condensate from the tube surface, thereby increasing the rate of heat transfer 2 to 3 times. For a horizontal bank of tubes the rate of heat transfer is higher when the stream of condensate from an upper tube flows down covering only a small fraction of the surface of the lower tube, reaching this tube at the horizontal diameter. More comprehensive data on boiling and vapour condensation, turbulent condensate film flow and heat transfer upon dropwise condensation can be found in textbook [4].

Typical Questions and Examples to Chapter Twenty Eight

1. Under what conditions do the processes of boiling and condensation take place?
2. Where do vapour bubbles form?
3. What is meant by nucleate boiling and film boiling?
4. What moment of boiling is called critical?
5. What equations are recommended for calculating the coefficient of heat transfer in a liquid undergoing nucleate boiling?
6. What are the different modes of condensation?
7. What affects the coefficient of heat transfer upon condensation?
8. Write down the equations of heat transfer for a vertical wall and horizontal plate.
9. Write down the criterion equations for heat transfer upon condensation.
10. How is the mass of the condensate determined?
11. How does the direction of vapour motion influence heat transfer?
12. How does the state of the surface influence heat transfer?

13. How do gas admixtures affect the rate of heat transfer in condensing vapours?

14. How is the rate of heat transfer influenced by the arrangement of heat-transfer surfaces in a condenser?

Example 28-1. Calculate the coefficient of heat transfer in boiling water and the quantity of steam produced in an evaporator in 1 h, if the total surface of the evaporator $F=5$ m². The temperature of the evaporator wall $t_w=156$ °C, steam pressure is 4.5 bar.

At the given pressure the saturation temperature $t_f=148$ °C. The heat of vaporization $r=2120.9$ kJ/kg; the difference between the wall-surface and steam temperatures $\Delta t=t_w-t_f=8$ °C.

The heat-transfer coefficient is determined from Eq. (28-3)

$$\alpha=46\,\Delta t^{2.33}p^{0.5}=46\times 8^{2.33}\times 4.5^{0.5}=12\,850 \text{ W/m}^2\cdot\text{deg}.$$

The quantity of heat transferred is equal to

$$Q=\alpha\,\Delta t F=12\,150\times 8\times 5=515\,000 \text{ W}=515 \text{ kW}.$$

The hourly production of steam in the evaporator

$$m=\frac{515\,000\times 3600}{2\,120\,900}=875 \text{ kg/h}.$$

Example 28-2. Determine the coefficient of heat transfer from vapour to the vertical tube of a condenser. The outside diameter of the tube $d=30$ mm, height $H=3$ m and the tube surface temperature $t_w=11$ °C. Saturated vapour condenses on the tube surface at a pressure $p=0.04$ bar and temperature $t_s=29$ °C.

The physical properties are determined at

$t_{av}=0.5(11+29)=20$ °C; $\varrho=998.2$ kg/m³;

$\lambda=0.515$ W/m·deg; $\nu=1.006\times 10^{-6}$ m²/s;

at $t_s=29$ °C the heat of vaporization $r=2432.3$ kJ/kg.

The heat-transfer coefficient is determined by Eq. (28-5)

$$\alpha_{vert}=1.14\sqrt[4]{\frac{9.81\times 998.2\times 2\,432\,300\times 0.515^3}{1.006\times 10^{-6}\times 3\times 18}}=3160 \text{ W/m}^2\cdot\text{deg}.$$

The quantity of heat transferred to the tube surface,

$$Q=\alpha F\,\Delta t=3160\times 3.14\times 0.03\times 3\times 18=16\,000 \text{ W}.$$

Dividing the obtained quantity of transferred heat by the heat of vaporization, we obtain the amount of condensate formed

$$m=\frac{Q}{r}=\frac{16\,000\times 3600}{2\,432\,300}=79 \text{ kg/h}.$$

Under the same conditions, for a horizontal tube we obtain

$$\alpha_{hor}=0.72\sqrt[4]{\frac{9.81\times998.2\times2\,432\,300\times0.513^3}{1.006\times10^{-6}\times0.03\times18}}=6320\ \text{W/m}^2\cdot\text{deg}.$$

The quantity of heat transferred to the tube surface,

$$Q=6320\times3.14\times0.03\times3\times18=32\,200\ \text{W}.$$

The quantity of condensate formed,

$$m=\frac{32\,200\times3600}{2\,432\,300}=158\ \text{kg/h}.$$

With a horizontal tube twice as much condensate will be produced, than with a vertical tube.

CHAPTER TWENTY NINE

THERMAL RADIATION HEAT TRANSFER

29-1. General Data on Thermal Radiation

Radiant energy originates at the expense of other forms of energy resulting from intricate molecular and intra-atomic processes. The nature of all rays is the same. They are electromagnetic waves propagated in space. The source of thermal radiation is the internal energy of a heated body. The amount of radiant energy depends mainly on the physical properties and temperature of the emitting body (emitter). Electromagnetic waves are distinguishable either by the wavelength or by the frequency in oscillations per second. Denoting the wavelength by λ, and the oscillation frequence by N, the propagation velocity in absolute vacuum for waves of all kinds is $w=\lambda N=300\,000$ Km/s.

Depending on wavelength λ, rays possess various properties. The rays of greatest interest to heat transfer are thermal rays which have a wavelength $\lambda=0.8\text{-}40\mu$m.

Radiation is inherent in all bodies. Every body emits and absorbs radiant energy continuously, if the temperature of the body is other than 0 K. There is always thermal-radiation heat transfer between bodies (having the same or different temperatures) arbitrarily arranged in space.

When bodies are in thermal equilibrium the quantity of emitted radiant energy is equal to the amount of absorbed radiant energy. The radiation spectrum of most solids and fluids (gases and liquids) is continuous. These bodies emit rays of all wavelengths from short to long.

Gases have a line radiation spectrum. Gases do not emit rays of all wavelengths. Radiation of this kind is referred to as *selective*, or *discontinuous, radiation*. The radiation of gases is of a volumetric nature.

Tests conducted by M. Melloni have shown that in emission from a solid not only the particles on the surface take part, but also a very thin layer of a certain thickness takes part. The total radiation from the surface of a body in all directions of a hemisphere and of all wavelengths is called *integral* or *total radiation* (Q).

The total radiation emitted per unit area in all directions of a hemisphere is called the *integral density of hemispherical radiation of a body*. It is measured in units of watts per square meter and denoted by

$$E=\frac{dQ}{dF},$$

where dQ is the element of radiation flux emitted by surface element dF.

Any body is capable not only of emitting rays, but also of reflecting them, absorbing them and passing rays incident from another body through itself. Denoting the total amount of incident radiant energy by Q, then a fraction of energy, equal to A, is absorbed by the body, a fraction, equal to R, is reflected, and a fraction, equal to D, passes through the body. It follows from this that

$$Q=Q_A+Q_R+Q_D,$$

or

$$A+R+D=1.$$

The quantity A is referred to as *absorptivity;* it represents the ratio of the absorbed radiant energy to the total energy incident on the body. The quantity R is called the *reflectivity;* it represents the ratio of reflected radiant energy to the total incident energy. The quantity D is referred to as *transmissivity; D* is the ratio of the radiant energy which passes through the body to the total incident energy. For the majority of bodies that are practically nontransparent (athermanous) to thermal radiation, $A+R=1$.

A surface which absorbs all rays incident upon it (i.e. $A=1$, $R=0$ and $D=0$) is called a *black body.* If a surface reflects all the rays incident upon it, it is called *absolutely white.* For such a surface $D=0$, $A=0$, $R=1$. If a body is *absolutely transparent* to thermal radiation, then $D=1$, $R=0$ and $A=0$. There are no absolutely black, white or transparent bodies in nature, nevertheless the concept of them is important for comparison with real surfaces.

Quartz is nontransparent to thermal rays, but it is transparent to light and ultraviolet rays. Rock salt is transparant to thermal rays and nontransparant to ultraviolet rays. Window pane is transparent to light rays and almost fails to pass ultraviolet and thermal rays. A white surface (fabric, paint) reflects only visible rays properly and absorbs heat rays as well as a black surface does. Thus, the ability of bodies to absorb or reflect heat rays depends mainly on the state of the surface, and not on its colour.

If a surface reflects rays according to the laws of geometrical optics, it is called a *mirror-like* (specular) surface. If a reflected incident ray splits into many rays going in all possible directions, the radiation is said to be *diffused* (this occurs, for instance, at the surface of chalk).

In investigating radiation fluxes, the distribution of the radiant energy, emitted by a black body in individual wavelengths of the spectrum, is very important. For each wavelength, at a definite temperature, there is a definite radiation intensity $I_{s\lambda}$. By the *radiation intensity*, or by the *spectral* (monochromatic) *intensity*, is meant the radiation flux of a body for wavelengths from λ to $\lambda+d\lambda$, reduced to the wavelength interval considered, $d\lambda$

$$I_{s\lambda}=\frac{dF_{s\lambda}}{d\lambda}, \tag{29-1}$$

where $I_{s\lambda}$ is the spectral intensity of black body radiation, W/m³.

29-2. Basic Law of Absorption

Solid and liquid bodies of finite thickness and also three- and polyatomic gases are capable of emitting and absorbing energy. If a ray of intensity I_{λ_1} is incident upon some body, it is partly absorbed and leaves the body on its opposite side with an intensity I_{λ_2}, less than I_{λ_1}. For a ray of a given wavelength the absorption coefficient is determined from equation

$$A_\lambda = \frac{I_{\lambda_1} - I_{\lambda_2}}{I_{\lambda_1}}. \tag{a}$$

Experimental studies show that the drop of intensity dI_λ is proportional to the initial intensity I_λ, the path length dx and depends on the properties of the body involved:

$$dI_\lambda = -kI_\lambda\, dx.$$

The minus sign on the right-hand side is an indication of the decreasing intensity. The proportionality factor k, which depends on the physical properties of the body, temperature and wavelength, is called the *absorption coefficient* for rays of a given wavelength; the dimension of the absorption coefficient k is 1/m.

Separating the variables, we obtain

$$\frac{dI_\lambda}{I_\lambda} = -k\, dx.$$

Integrating the above equation with respect to x between the limits $x=0$ and $x=s$, we find that

$$\int_{I_{\lambda_1}}^{I_{\lambda_2}} \frac{dI}{I_\lambda} = -\int_0^s k\, dx,$$

so for $k=\text{const}$

$$\ln \frac{I_{\lambda_2}}{I_{\lambda_1}} = -ks \quad \text{or} \quad \frac{I_{\lambda_2}}{I_{\lambda_1}} = e^{-ks} \quad \text{and} \quad I_{\lambda_2} = I_{\lambda_1} e^{-ks}.$$

It follows that the absorption coefficient

$$A_\lambda = \frac{I_{\lambda_1} - I_{\lambda_2}}{I_{\lambda_1}} = \frac{I_{\lambda_1} - I_{\lambda_1} e^{-ks}}{I_{\lambda_1}} = 1 - e^{-ks} = 1 - \frac{1}{e^{ks}}. \tag{29-2}$$

The derived equation shows that A_λ depends on the absorption coefficient k and the thickness s of the layer of the body. For a thickness $s=0$, the coefficient $A_\lambda = 0$, i.e. absorption of radiation can take place only in a layer of the substance having finite thickness. If $s=\infty$, then $A_\lambda = 1$, i.e. a layer of great thickness completely absorbs the rays just as a black body does. The coefficient A_λ is also influenced by the proportionality factor k. When k is large radiation is absorbed only in a thin surface layer. Accordingly, the state of the surface of a body greatly affects its ability to absorb and ability to emit. If $k=0$, then $A_\lambda = 0$.

29-3. Basic Laws of Thermal Radiation of Heat Transfer

Planck's law. The intensity of black body radiation, $I_{s\lambda}$, depends on the temperature and the wavelength as does the radiation of any real body, I_λ.

At a given temperature a black body emits rays of all wavelengths, from $\lambda=0$ to $\lambda=\infty$, but the energy distribution differs along the spectrum.

With increasing wavelength the energy of rays increases, reaches a maximum at some wavelength, then decreases. In addition, the energy of ray of a given wavelength increases with the temperature of the emitting body, as illustrated in Fig. 29-1.

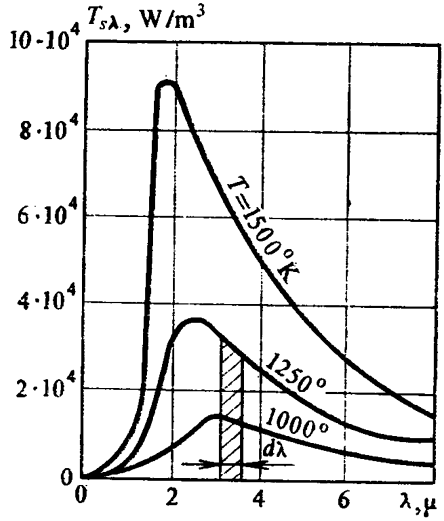


FIG. 29-1

Proceeding from the electromagnetic nature of radiation and making use of the concept of energy quanta, M. Planck established theoretically the following law, governing the variation of black body radiation, depending on the temperature and the intensity wavelength

$$I_{s\lambda}=\frac{c_1\lambda^{-5}}{e^{\frac{c_2}{\lambda T}}-1}, \qquad (29\text{-}3)$$

where e = base of natural logarithms;
$c_1 = 3.74\times10^{-16}$ W·m^2=Planck first constant;
$c_2 = 1.44\times10^{-2}$ m·deg=Planck second constant;
λ = wavelength, m;
T = absolute temperature of emitting body, K.

It can be seen from Fig. 29-1 that for a given temperature the radiation intensity $I_{s\lambda}$ increases from zero at $\lambda=0$ to its maximum value at a certain

wavelength, then decreases to zero at $\lambda=\infty$. With increasing temperature the radiation intensity for each wavelength increases.

In addition, as can be seen from Fig. (29-1), when the temperature rises the maxima of the curves shift to side of short waves. The length of wave λ_{ms}, mm, corresponding to the maximum value $I_{s\lambda}$, is determined by Wien's displacement law

$$\lambda_{ms}=2.9/T \tag{29-4}$$

When the temperature rises λ_{ms} decreases which follows from the law.

Stefan-Boltzmann law. On the basis of test results J. Stefan established in 1879 that the intensity of black body radiation is directly proportional to the fourth power of absolute temperature: $u=aT^4$. In 1884, L. Boltzmann obtained this law theoretically. Starting from the second law of thermodynamics and assuming the existence of radiation pressure.

To derive the analytical expression of Stefan-Boltzmann law, let us make use of the thermodynamic identity

$$T\,ds=dU+p\,dV,$$

from which, as has been shown in Chapter X [Eq. (10-7)], it follows that

$$T\left(\frac{\partial p}{\partial T}\right)_V=\left(\frac{\partial U}{\partial V}\right)_T+p, \tag{a}$$

where p = radiation pressure;
U = energy of equilibrium radiation from volume V.

In accordance with the laws of electrodynamics, considering equilibrium radiation as a photon gas, radiation pressure can be expressed as follows:

$$p=\frac{u}{3}, \tag{b}$$

where $u=U/V$ is the energy density of equilibrium radiation. Then, by simple transformations, remembering that $U=uV$, Eq. (a) takes the form

$$\frac{T\,du}{dT}=4u,$$

or

$$\frac{du}{u}=4\left(\frac{dT}{T}\right).$$

Integrating and finding the antilogarithm of the integration result, we obtain

$$u=aT^4. \tag{c}$$

Eq. (c) is the mathematical expression of the *Stefan-Boltzmann* law, i.e. the energy density of equilibrium radiation is proportional to the fourth power of the absolute temperature.

The constant a is not determined thermodynamically; test results indicate that $a=7.64\times10^{-16}$ J/m³·K⁴.

The energy density of equilibrium radiation u is related to the density of integral radiation E by the ratio

$$u=\frac{4E}{c}, \tag{d}$$

where c is the velocity of photons, equal to the velocity of light in a vacuum.

Substituting into Eq. (c) the value of u from Eq. (d) we obtain

$$E=\frac{ac}{4}T^4,$$

or

$$E=\sigma T^4, \tag{29-5}$$

where σ is the Stefan-Boltzmann constant for black body radiation.

$$\sigma=\frac{ac}{4}=5.77\times10^{-8}\ \text{W/m}^2\cdot\text{K}^4.$$

The mathematical statement of the Stefan-Boltzmann law can also be obtained from Planck's law. The thermal radiation emitted from a unit surface of a black body in the wavelength interval from λ to $\lambda+d\lambda$ can be determined from the equation

$$dE_s=I_{s\lambda}\,d\lambda.$$

In Fig. 29-1 the elementary area bounded by the curve $T=$const, base $d\lambda$ and ordinates λ and $\lambda+d\lambda(I_{s\lambda})$ determines the amount of radiant energy dE_s and is referred to as the *density of total black body radiation* for wavelengths $d\lambda$. But the entire area between an arbitrary curve $T=$const and the axis of abscissae is equal to the total radiation of a black body between the limits $\lambda=0$ and $\lambda=\infty$ at the given temperature, or

$$E_s=\int_{\lambda=0}^{\lambda=\infty} I_{s\lambda}\,d\lambda.$$

Substituting into the derived equation Planck's law, we obtain

$$E_s=\int_{\lambda=0}^{\lambda=\infty}\frac{c_1\lambda^{-5}}{e^{c_2/\lambda T}-1}\,d\lambda$$

and, integrating, we find that

$$E_s=\sigma_s T^4. \tag{29-5'}$$

Thus, the hemispherical total emissive power (heat flux) of a black body is directly proportional to the fourth power of the absolute temperature.

In technical literature the Stefan-Boltzmann law is usually presented in the following form:

$$E_s = C_s\left(\frac{T}{100}\right)^4 \tag{29-6}$$

where C_s is the emission coefficient of a black body, equal to 5.77 W/m^2·K^4 [5].

A more convenient formula can be recommended for practical calculations; replacing W/m^2 by kW/m^2, we obtain

$$E_s = 57.7\left(\frac{T}{1000}\right)^4, \text{ kW/m}^2.$$

All real bodies used in practical engineering are black bodies and at a given temperature they emit less energy than a black body does. The emission of real bodies also depends on temperature and wavelength (with $A_\lambda \cong \text{const} < 1$). To make the laws governing black body radiation applicable to real bodies, the concept of the grey body and grey-body radiation is introduced. Grey body radiation is radiation which, by analogy with black body radiation, has a continuous spectrum, but for which the intensity I_λ of rays for each wavelength λ at any temperature is a constant fraction of the corresponding intensity of black body radiation $I_{s\lambda}$ at the same wavelength (Fig. 29-2). Consequently,

$$\frac{I_\lambda}{I_{s\lambda}} = \varepsilon = \text{const}. \tag{29-7}$$

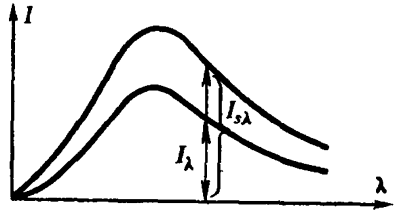


FIG. 29-2

The quantity ε is called the *spectral emissivity*. It depends on the physical properties of bodies. The emissivity of grey bodies is always smaller than unity.

Most real solid bodies may be considered with certain degree of accuracy to be grey bodies and the radiation emitted by them to be grey-body radiation.

The total radiation intensity of a grey body is equal to

$$E = \int_{\lambda=0}^{\lambda=\infty} I_\lambda \, d\lambda.$$

However $I_\lambda = \varepsilon I_{s\lambda}$, therefore

$$E = \varepsilon \int_{\lambda=0}^{\lambda=\infty} I_{s\lambda} \, d\lambda = \varepsilon E_s = \varepsilon C_s\left(\frac{T}{100}\right)^4 = C\left(\frac{T}{100}\right)^4. \tag{29-8}$$

The total radiation intensity of a grey body is a fraction ε of the total radiation intensity of a black body.

The quantity $C=\varepsilon C_s$ W/m²K⁴ is referred to as the *emission coefficient of a grey body.* In the general case for real bodies the quantity C depends not only on the physical properties of a body, but also on the state of its surface (or on its roughness) and also on the temperature and wavelength. The values of the emission coefficients and emissivities of bodies are taken from Table 29-1.

Kirchhoff's law. The radiation energy and energy of absorption of any body depend on temperature and wavelength. Various bodies have different values for E and A. The two values are related by Kirchhoff's law. Consider heat exchange by radiation between two parallel plates at different temperatures, with the first plate being a black body at a temperature T_s and the second—a grey body at a temperature T. The distance between the two plates is considerably smaller than their dimensions so that the radiation emitted from each of them is necessarily incident upon the other.

TABLE 29-1

Normal Total Emissivity of Various Materials

Material	t, °C	ε
Aluminium, polished	50-500	0.04-0.06
Bronze	50	0.1
Sheet iron, galvanized, bright	30	0.23
Tin, old, white	20	0.28
Gold, polished	200-600	0.02-0.03
Brass, dull	20-350	0.22
Copper, polished	50-100	0.02
Nickel, polished	200-400	0.07-0.09
Tin, bright	20-50	0.04-0.06
Silver, polished	200-600	0.02-0.03
Steel plate, rolled	50	0.56
Steel, oxidized	200-600	0.8
Steel, heavily oxidized	500	0.98
Cast iron	50	0.81
Asbestos cardboard	20	0.96
Wood, planed	20	0.8-0.9
Brick, refractory	500-1000	0.8-0.9
Brick, chamotte	1000	0.75
Brick, rough	20	0.88-0.93
Lacquer, black, dull	40-100	0.96-0.98
Lacquer, white	40-100	0.8-0.95
Oil colours, various	100	0.92-0.96
Lampblack	20-400	0.95
Glass	20-100	0.91-0.94
Enamel, white	20	0.9

In accordance with the Stefan-Boltzmann law, the second surface emits energy E to the first surface. This is fully absorbed by the black surface. In its turn, the first surface emits to the second surface, energy E_s. A fraction of this energy $E_s A$ is absorbed by the grey surface, and the remaining energy $(1\text{-}A)E_s$ is reflected to the first surface and is fully absorbed by it. In these conditions the grey surface receives an amount $E_s A$ of radiant energy and gives off an amount E. Consequently, the heat balance equation has the following appearance

$$Q=E-E_s A.$$

With temperatures T and T_s equal the heat flux Q is equal to zero. From this it follows that

$$E=E_s A, \quad \text{or} \quad \frac{E}{A}=E_s=\frac{E_s}{A_s}=C_s\left(\frac{T}{100}\right)^4. \tag{29-9}$$

Since the second body can be replaced by any other body, Eq. (29-9) is valid for an arbitrary body and describes Kirchhoff's law. With thermodynamic equilibrium the *ratio of the reflectivity of a body to its absorptivity is the same for all grey bodies at equal temperatures and is equal to the emissive ability of a black body at the same temperature.*

This ratio can be obtained from thermodynamics.

Let an enclosure accommodate two bodies: a black body and a grey one. According to the second law of thermodynamics, thermal equilibrium requires that each body should emit and absorb the same amounts of radiant energy. Non-fulfilment of this condition would lead to the breaking of the temperature equality between the surface of the cavity and the bodies. Radiant energy $I_{s\lambda}\,d\lambda$ falls on unit area of the black body that is completely absorbed by it and simultaneously the same amount of radiant energy is emitted by the black body. It follows that $I_{s\lambda}\,d\lambda A_s=E_{s\lambda}\,d\lambda$ and $I_{s\lambda}=E_{s\lambda}$, since $A_s=1$. A unit surface area of the grey body absorbs only a fraction of the radiant energy $I_{s\lambda}\,d\lambda$ incident upon it. If the absorptivity of the body is equal to A_λ, then the body will absorb an amount, $I_{s\lambda}A_\lambda\,d\lambda$ of energy, emitting the same amount of energy. The radiant energy of the grey body is $E_\lambda\,d\lambda$. It follows from this that $I_{s\lambda}A_\lambda d\lambda=E_\lambda\,d\lambda$.

Substituting into the last equation the value of $I_{s\lambda}$ for a black body, we obtain the Kirchhoff law

$$E_{s\lambda}A_\lambda\,d\lambda=E_\lambda\,d\lambda, \quad \text{or} \quad E_{s\lambda}=\frac{E_\lambda}{A_\lambda}.$$

It follows from Kirchhoff's law that if the absorptivity of a body is small, its *emissive ability* is also insignificant (as for instance with polished metals). A black body, possessing a high absorptivity, also has a maximum *emissive ability.*

The Kirchhoff law is also valid for spectral (monochromatic) radiation. The ratio of the radiation intensity of a body at a definite wavelength is the same for all bodies at the same temperature and equal numerically to the

radiation intensity of a black body at the same wavelength and temperature, i.e. the ratio is only a function of wavelength and temperature

$$\frac{E_\lambda}{A_\lambda}=\frac{I_\lambda}{A_\lambda}=E_{s\lambda}=I_{s\lambda}=f(\lambda, T). \tag{29-10}$$

Hence a body emitting energy at some wavelength is capable of absorbing that energy at the same wavelength. If a body fails to absorb energy in some part of the spectrum, it also does not emit energy in that part of the spectrum.

It also follows from the Kirchhoff law that at the same temperature the emissivity of a grey body, ε, is equal numerically to the absorption coefficient A

$$\varepsilon=\frac{I_\lambda}{I_{s\lambda}}=\frac{E}{E_s}=\frac{C}{C_s}=A.$$

Lambert cosine law. The energy emitted by a body propagates in space with various intensities. The law giving the dependence of radiation intensity on direction is known as *Lambert's cosine law.*

According to Lambert's cosine law the amount of energy radiated from an elementary area dF_1 in the direction of area dF_2 is proportional to the product of the energy emitted along the normal dQ_n, the solid angle $d\omega$ and cos φ, where φ is the angle enclosed between the direction of radiation and the normal (Fig. 29-3*a*)

$$d^2Q_\varphi=dQ_n\, d\omega \cos\varphi,$$

or

$$d^2Q_\varphi=E_n\, dF_1\, d\omega \cos\varphi, \tag{29-11}$$

where E_n is the radiant energy emitted in the direction of the normal.

It follows that maximum energy is emitted in the direction perpendicular to the emitting surface, i.e. when $\varphi=0$. The amount of energy emitted decreases with increasing φ and is equal to zero when $\varphi=90°$.

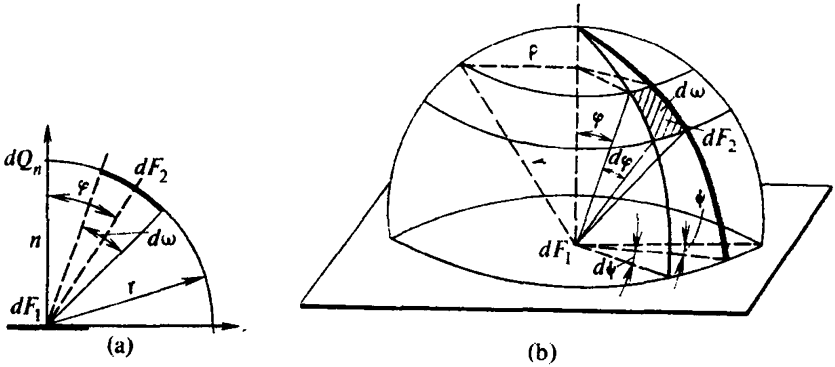


FIG. 29-3

To determine the quantity E_n, Eq. (29-11) must be integrated over the surface of the hemisphere lying on top of elementary area dF_1 (Fig. 29-3*b*).

The solid angle $d\omega$ is that at which the elementary area dF_2 on the surface of a sphere with radius r is seen from any point of elementary area dF_1. It follows from this that

$$d\omega = \frac{dF_2}{r^2},$$

or

$$d\omega = \sin\varphi \, d\psi \, d\varphi,$$

where φ = angle complementary to the angle of latitude;
ψ = angle of latitude.

Substituting the expression obtained into Eq. (29-11), we get

$$d^3Q_\varphi = E_n \, dE_1 \sin\varphi \, d\psi \, d\varphi \cos\varphi.$$

Integrating the above expression over the surface of a hemisphere, i.e. between the limits of variation of angle φ from 0 to $\pi/2$ and of angle ψ from 0 to 2π, we find the energy emitted by elementary area dF_1, within the limits of the hemisphere, equal to $E\,dF_1$. Hence,

$$E\,dF_1 = E_n\,dF_1 \int_{\psi=0}^{2\pi} d\psi \int_{\varphi=0}^{\pi/2} \sin\varphi\cos\varphi\,d\varphi = \pi E_n\,dF_1,$$

whence

$$E_n = \frac{E}{\pi} = \frac{1}{\pi} C \left(\frac{T}{100}\right)^4 = \frac{\varepsilon}{\pi} C_0 \left(\frac{T}{100}\right)^4.$$

It follows from the above equation that the radiant energy in the normal direction is π times smaller than the hemispherical total emissive power of a black body (or grey body) determined by the Stefan-Boltzmann law. Hence Lambert's cosine law (Eq. 29-11) takes the form

$$d^2Q_\varphi = \frac{\varepsilon}{\pi} C_0 \left(\frac{T}{100}\right)^4 d\omega \cos\varphi \, dF_1. \qquad (29\text{-}11')$$

Equation (29-11′) was derived for the total radiation from elementary area dF_1, but it remains also valid for monochromatic radiation or spectral emission.

Formula (29-11′) is the main equation for calculating the thermal radiation heat transfer between finite surfaces.

The Lambert cosine law is true for black or grey bodies, and for bodies where there is diffused radiation in the range $\varphi = 0 - 60°$ only. The Lambert cosine law is not applicable to polished surfaces.

29-4. Radiation Heat Transfer Between Solids

Parallel Plates

The Stefan-Boltzmann law enables the density of emitted radiation E_1 which originates in the surface layer of a body to be determined. This radiation is completely determined by the body's temperature and its physical properties. If a body takes part in the mutual exchange of thermal radiation with other bodies, then we may suppose that an amount E_{in} of external radiant energy is incident on the body. A fraction of the incident radiant energy, AE_{in}, is absorbed by the body and is converted into internal energy. The remaining radiant energy, an amount RE_{in}, is reflected from the body. The sum of the radiant energy emitted from the body and the energy reflected from the surface of the body is called the *outgoing radiation* or the *radiation leaving the surface* E_{leav}

$$E_{leav}=E_{em}+RE_{in}=E_{em}+(1-A)E_{in}.$$

The outgoing radiation depends not only on the physical properties and temperature of a given body, but also on the physical properties, temperature and radiation spectrum of the other surrounding bodies. In addition, it depends on the shape and size of bodies and their mutual arrangement in space. In consequence of this the physical properties of the outgoing radiation and the emitted radiation are not the same and their radiation spectra differ.

For a black body $E_{leav}=E_{em}$, since $E_{ref}=0$.

Consider the exchange of thermal radiation between two parallel grey plates separated by a transparent (diathermanous) medium. The dimensions of the plates are considerably larger than the distance between them, so that the radiation from one of them is completely incident upon the other. The plate surfaces obey the Lambert cosine law. Let us denote: the plate temperatures by T_1 and T_2; the absorption coefficients by A_1 and A_2; the emitted radiations of the plates, determined by means of the Stefan-Boltzmann law, by E_1 and E_2; the radiations leaving the plates by $E_{1\,leav}$ and $E_{2\,leav}$ and the emission coefficients by C_1 and C_2. Assume that $T_1>T_2$.

The first plate emits radiant energy upon the second; the second plate absorbs a fraction of that energy, and reflects a fraction of it back to the first, where again the first surface absorbs a fraction and radiates a fraction to the second, etc.

The total radiation flux from the first plate, consisting of the emitted radiation E_1 and the reflected radiation from the second plate, equal to $(1-A_1)E_{2\,leav}$, is found from equation

$$E_{1\,leav}=E_1+(1-A_1)E_{2\,leav}.$$

By analogy, we find the total, or net, radiation from the second plate

$$E_{2\,leav}=E_2+(1-A_2)E_{1\,leav}.$$

Solving the two equations with respect to $E_{1\,leav}$ and $E_{2\,leav}$, we obtain

$$E_{1\,leav}=\frac{E_1+E_2-A_1E_2}{A_1+A_2-A_1A_2};\qquad E_{2\,leav}=\frac{E_1+E_2-A_2E_1}{A_1+A_2-A_1A_2}.$$

The thermal radiation incident upon the second plate is found from equation

$$q=E_{1\,leav}-E_{2\,leav}.$$

Substituting the values of $E_{1\,leav}$ and $E_{2\,leav}$ and carrying out corresponding transformations, we obtain

$$q=\frac{A_2E_1-A_1E_2}{A_1+A_2-A_1A_2}=\frac{A_2A_1C_s\left(\frac{T_1}{100}\right)^4-A_1A_2C_s\left(\frac{T_2}{100}\right)^4}{A_1+A_2-A_1A_2},$$

or

$$q=\frac{\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4}{\frac{A_1}{A_1A_2C_s}+\frac{A_2}{A_1A_2C_s}-\frac{A_1A_2}{A_1A_2C_s}}=\frac{\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4}{\frac{1}{C_1}+\frac{1}{C_2}-\frac{1}{C_s}}.$$

Thus, the radiation heat transfer between parallel surfaces is determined by means of the equation

$$Q=C_{red}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]F, \tag{29-12}$$

where $C_{red}=\dfrac{1}{\frac{1}{C_1}+\frac{1}{C_2}-\frac{1}{C_s}}$ is referred to as the *reduced emission coefficient.*

In calculations C_{red} can be replaced with the reduced emissivity of a system of bodies presented in the following form:

$$C_{red}=\varepsilon_{red}C_s,$$

where ε_{red} is the reduced emissivity of a system:

$$\varepsilon_{red}=\frac{1}{\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}-1}, \tag{29-13}$$

then

$$q=\frac{C_s\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]}{\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}-1}.$$

Radiation Heat Transfer Between Bodies One of Which Is Situated Inside the Other

Problems in radiation heat transfer often have to be solved where one body is situated inside the other, as illustrated in Fig. 29-4. The surface of the internal body is convex and the inside surface of the external body is concave. We call the internal body the first body, the external body the second body.

Denote the quantities of the internal body by $A_1, C_1, \varepsilon_1, T_1, F_1$ and of the external body—by $A_2, C_2, \varepsilon_2, T_2, F_2$. In distinction to radiation heat transfer between prallel plates, in this case only a fraction φ of the radiation leaving the second body is incident upon it. The remaining fraction of the radiant energy $(1-\varphi)$ is incident upon the surface of the second body.

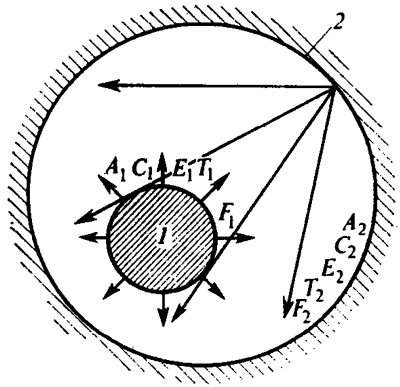


FIG. 29-4

The radiation leaving the surface of the first body consists of the emitted radiation and radiation reflected, from the second body

$$E_{1\,leav}=E_1F_1+(1-A_1)\varphi E_{2\,leav}. \qquad \text{(a)}$$

The radiation leaving the surface of the second body consists of emitted radiation, radiation reflected from the first body and reflected emitted radiation, namely

$$E_{2\,leav}=E_2F_2+(1-A_2)E_{1\,leav}+(1-A_2)(1-\varphi)E_{2\,leav}. \qquad \text{(b)}$$

The net radiation exchanged between the two bodies is

$$Q=E_{1\,leav}-E_{2\,leav}.$$

Solving together Eqs. (a) and (b) and substituting $E_{1\,leav}$ and $E_{2\,leav}$ into the last equation, we obtain*

$$Q=\frac{1}{\dfrac{1}{C_1}+\dfrac{F_1}{F_2}\left(\dfrac{1}{C_2}-\dfrac{1}{C_s}\right)}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]F_1 \qquad (29\text{-}14)$$

Denote the quantity $\dfrac{1}{\dfrac{1}{C_1}+\dfrac{F_1}{F_2}\left(\dfrac{1}{C_2}-\dfrac{1}{C_s}\right)}$ by C_{red}.

---

* It is assumed that $\varphi=\dfrac{F_1}{F_2}$. This can be proved by considering the limiting case when $T_1=T_2$.

Then, radiation heat transfer between two bodies, one of which lies inside the other, is determined by the equation

$$Q = C_{red} F_1 \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]. \tag{29-15}$$

If the quantity C_{red} is replaced in calculations by the reduced emissivity of a system of bodies, then the equation of radiation heat transfer acquires the following appearance:

$$Q = \frac{1}{\frac{1}{\varepsilon_1} + \frac{F_1}{F_2}\left(\frac{1}{\varepsilon_2} - 1 \right)} C_s F_1 \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]. \tag{29-16}$$

If the surface F_1 is small compared with surface F_2, then the ratio $\frac{F_1}{F_2}$ approaches zero and $C_{red} = C_1$, and the radiation heat-transfer equation becomes

$$Q = C_1 F_1 \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]. \tag{29-17}$$

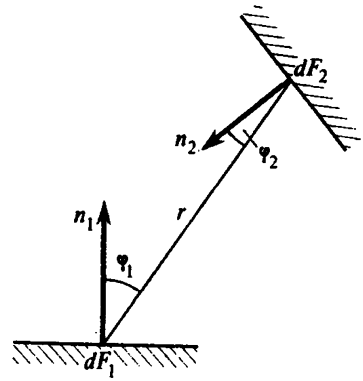


FIG. 29-5

Radiation Heat Transfer Between Bodies Arbitrarily Arranged in Space

It is very difficult to derive analytically the equation of radiation heat transfer between two bodies arbitrarily arranged in space, and the problem can be solved for private cases only.

The amount of heat transferred by radiation between two bodies arbitrarily arranged in space (Fig. 29-5) is calculated by formula

$$Q = \frac{C_1 C_2}{C_s} \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right] \int_{F_1} dF_1 \int_{F_2} \frac{\cos \varphi_1 \cos \varphi_2}{\pi r^2} dF_2. \tag{29-18}$$

where $\frac{C_1 C_2}{C_s}$ = *reduced emission coefficient for the given system of bodies;*

$\int_{F_1} dF_1 \int_{F_2} \frac{\cos \varphi_1 \cdot \cos \varphi_2}{\pi r^2} dF_2$ = *angle* (configuration, shape, view) *factor.*

The angle factor is geometrical characteristic and it depends on the size, shape of the two emitting bodies and on their mutual arrangement. Calculation of the angle factor involves great mathematical difficulties even for the simplest cases, and so it is determined graphically. When solving problems in radiation heat transfer, the angle factor is usually taken from tables.

29-5. Radiation Heat Transfer with Screens

In various engineering applications it is quite often necessary to reduce the quantity of heat transferred by thermal radiation. For instance, workers must be protected from the effect of thermal rays in workshops where there are high-temperature surfaces. In other cases it is necessary to protect wooden parts of buildings from radiant energy so as to prevent ignition; it is necessary to guard thermometers from thermal radiation, for, otherwise, the thermometers would show erroneous readings. Hence whenever it is necessary to reduce the amount of heat transferred by thermal radiation, screens are installed. The usual type of screen is a thin metal sheet with a high reflectivity. The temperatures of both surfaces of the screen may be assumed to be equal.

Consider the effect of a screen between two flat infinite parallel surfaces, where the amount of heat transferred by convection can be ignored. The surfaces of the walls and the screen are assumed to be similar. The wall temperatures T_1 and T_2 are maintained constant, with $T_1 > T_2$. The emission coefficients of the walls and screen are assumed to be equal to each other. Then, the reduced coefficients of emission between the wall surfaces in the absence of a screen, between the first surface and the screen, and between the screen and the second surface are all equal to one another.

The heat flux transferred from the first surface to the second (in the absence of the screen) is determined from equation

$$q_0 = C_{red}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right].$$

The heat flux transferred from the first surface to the screen is found from the formula

$$q_1 = C_{red}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_{sc}}{100}\right)^4\right],$$

and the flux from the screen to the second surface—by equation

$$q_2 = C_{red}\left[\left(\frac{T_{sc}}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right].$$

Under steady-state heat-transfer conditions $q_1 = q_2$, therefore

$$C_{red}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_{sc}}{100}\right)^4\right] = C_{red}\left[\left(\frac{T_{sc}}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right],$$

whence

$$\left(\frac{T_{sc}}{100}\right)^4 = \frac{1}{2}\left[\left(\frac{T_1}{100}\right)^4 + \left(\frac{T_2}{100}\right)^4\right].$$

Substituting the temperature of the screen obtained into any of the equations, we get

$$q_{1\text{-}2} = \frac{1}{2} C_{red}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right].$$

Comparing the first and the last equations, we find that under the assumed conditions the use of a screen diminishes the rate of heat transfer by radiation by half:

$$q_{1\text{-}2}=\frac{1}{2}q_0. \tag{29-19}$$

It can be shown that two screens will diminish the quantity of heat transferred by radiation to one third, three screens to one fourth, etc. The amount of heat transferred by thermal radiation is reduced very effectively by using screens made from polished metal, when

$$q_1=0.5\left(\frac{C'_{red}}{C_{red}}\right)q_0, \tag{29-20}$$

where C'_{red} = reduced coefficient of emission between a surface and a screen;

C_{red} = reduced coefficient of emission between surfaces.

29-6. Radiation from Gases

Radiation from gases differs essentially from the radiation from solids. Monoatomic and diatomic gases have a negligibly small emissive ability and absorptivity. These gases are considered to be transparent or to heat rays diathermanous. Triatomic (CO_2 and H_2O) and polyatomic gases have a considerable emissive ability and, consequently, also a high absorptivity. At high temperatures the emission, from the triatomic gases formed by the combustion of fuel is important in heat-exchange equipment. In distinction to the emission from grey bodies, the radiation spectra of triatomic gases have a sharply pronounced selective nature. These gases absorb and emit radiant energy only in certain intervals of wavelengths in different parts of the spectrum (Fig. 29-6). For rays of other wavelengths these gases are

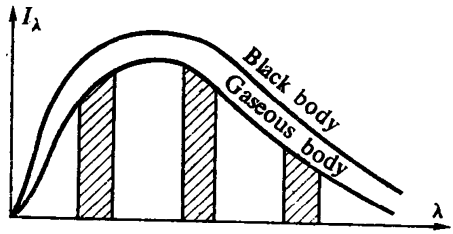


FIG. 29-6

transparent. When a ray with a given wavelength encounters a layer of gas capable of absorbing rays of this wavelength, it is partially absorbed. It passes partly through the gas and leaves the layer of gas with an intensity less than the original intensity. A thick layer of gas is able to absorb a ray almost completely. Also, the absorptivity of a gas depends on its partial

pressure, or number of molecules and temperature. The radiation from gases, and the absorption of radiant energy in gases occurs over the entire volume.

The absorption coefficient of a gas can be calculated from the following relationship

$$A_\lambda = f(T_g,\ p,\ s)$$

or with the aid of Eq. (29-2)

$$A_\lambda = 1 - \frac{1}{e^{ks}}.$$

The thickness of the layer of gas, s, depends on the form of the body and is determined as the mean beam length from Table 29-2.

TABLE 29-2

Mean Beam Length for Gas Filled Volumes of Different Shape

Shape of Volume filled with gas	l
Cylinder, height equal to diameter, radiation incident upon side wall	$0.6d$
Cylinder, height $h=\infty$	$0.9d$
Sphere, diameter d	$0.6d$
Flat parallel layer of gas with thickness h and infinite diameters	$1.8h$
Cube with side h	$0.6h$
Bank of tubes:	
tubes in triangular arrangement spaced at a distance $l=d$ apart	$2.8l$
tubes in triangular arrangement, $l=2d$	$3.8l$
tubes in square arrangement, $l=d$	$3.5l$

The pressure of combustion gases is usually assumed to be 1 bar, therefore, the partial pressure of triatomic gases in a mixture of gases are determined by equations $p_{CO_2}=r_{CO_2}$ and $p_{H_2O}=r_{H_2O}$, where r is the volume fraction of the gas in the mixture.

The mean wall temperature is calculated by equation

$$T_w = \frac{T'_w + T''_w}{2}, \tag{29-21}$$

where T'_w = temperature of channel wall at the gas inlet;
T''_w = temperature of channel wall at the gas outlet.

The mean temperature of gas is determined by formula

$$T_g = \frac{T'_w + T''_w}{2} \pm \frac{(T'_g - T'_w) - (T''_g - T''_w)}{2.3 \log \dfrac{(T'_g - T'_w)}{(T''_g - T''_w)}}, \tag{29-22}$$

where T'_g = gas temperature at the inlet to the channel;
T''_g = gas temperature at the outlet from the channel;

the plus sign is taken for cooling, and the minus sign when the gas is heated in the channel.

Calculations of heat transfer by radiation between a gas and walls of a channel are very intricate and are done with the aid of a number of charts and tables. A simpler and quite dependable method has been elaborated by A. Schack who suggested the following formulae determining the emission from gases into a medium at a temperature 0 K:

$$q_{CO_2} = 4.07 \sqrt[3]{ps} \left(\frac{T}{100}\right)^{3.5}, \tag{29-23}$$

$$q_{H_2O} = 40.7 p^{0.8} s^{0.6} \left(\frac{T}{100}\right)^{3}, \tag{29-24}$$

where p = partial pressure of gas, bar;
s = mean thickness of gas layer, m;
T = mean temperature of gases and wall, K.

An analysis of the above equations shows that the emissive ability of gases does not obey the Stefan-Boltzmann law. The emission from water vapour is proportional to T^3, and the emission from carbon dioxide—to $T^{3.5}$.

The same formulae are used to calculate the amount of heat absorbed by the gases due to radiation from the walls of the channel, but then the mean temperature of the gases is replaced in the formulae by the mean temperature of the channel walls.

Thus, the amount of heat transferred to the walls of a channel due to heat exchange by radiation between gases and the wall is found from equation

$$q_{rad} = (q_g - q_w), \tag{29-25}$$

where q_g = amount of heat emitted from carbon dioxide and water vapour at the mean gas temperature;
q_w = quantity of heat absorbed by carbon dioxide and water vapour at the mean temperature of channel walls.

The obtained total rate of heat transfer by radiation q_{rad} is used to determine the coefficient of heat transfer by radiation

$$\alpha_{rad} = \frac{q_{rad}}{T_g - T_w} \tag{29-26}$$

Many authors recommend calculating the radiation from gases by the Stefan-Boltzmann law.

The equation for heat transfer by radiation between a gas and the wall of a channel then acquires the following appearance:

$$q_{rad} = \varepsilon'_w C_s \left[\varepsilon_g \left(\frac{T_g}{100}\right)^4 - \varepsilon'_g \left(\frac{T_w}{100}\right)^4\right], \tag{29-27}$$

where $\varepsilon'_w = \frac{\varepsilon_w + 1}{2}$ = effective emissivity of channel walls taking into account the radiation from the gas;

C_s = emission coefficient of a black body, equal to 5.77, W/m²·K⁴;

$\varepsilon_g = \frac{q_g}{q_s}$ is the ratio of the radiant energy emitted from a gas to the radiant energy emitted from a black body relative to 1 m² of surface; ε_g is determined by formula

$$\varepsilon_g = \varepsilon_{CO_2} + \beta\varepsilon_{H_2O} - \Delta\varepsilon_g$$

where quantities ε_{CO_2}, ε_{HO_2} and β are determined from the graphs in Figs. 29-7, 29-8 and 29-9;

$\Delta\varepsilon_g$ = correction allowing for mutual absorption of radiant energy by the gases; for flue gases this correction amounts to from 2 to 4 per cent, and so is usually ignored;

β = correction factor, allowing for the stronger effect of partial pressure, compared with the influence of the thickness of the gas layer;

T_g = mean gas temperature, K;

$\varepsilon'_g = \varepsilon'_{CO_2} + \beta\varepsilon'_{H_2O}$ = absorptivity of gas at the mean temperature of channel walls, determined from the same charts;

T_w = mean temperature of channel walls, K.

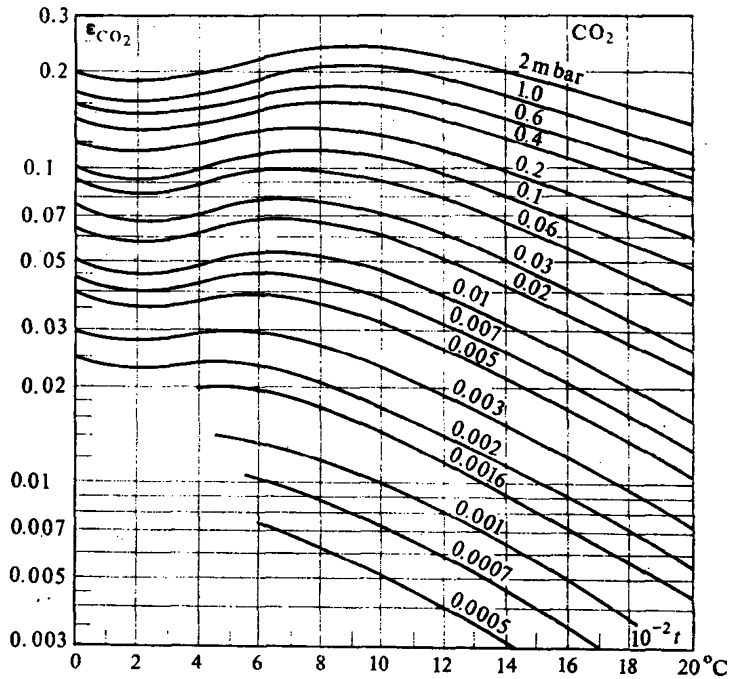


FIG. 29-7

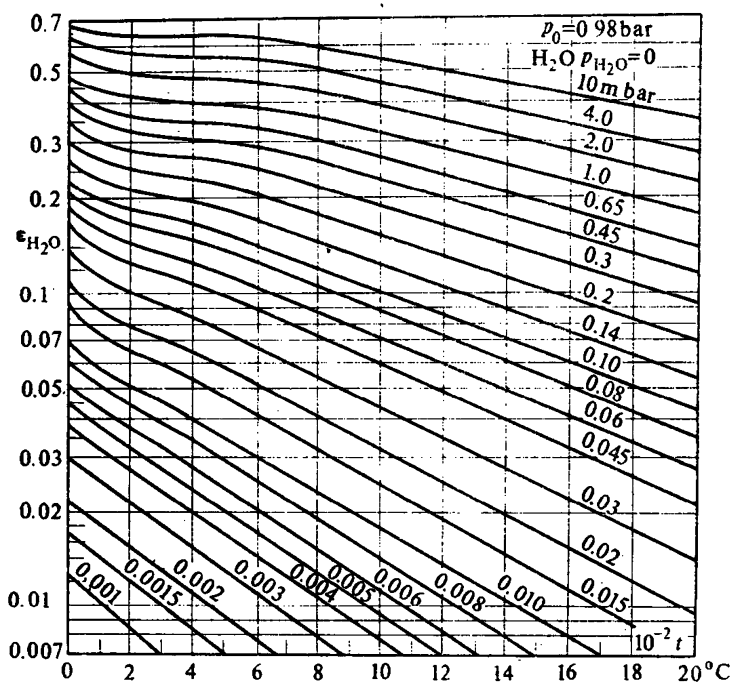


FIG. 29-8

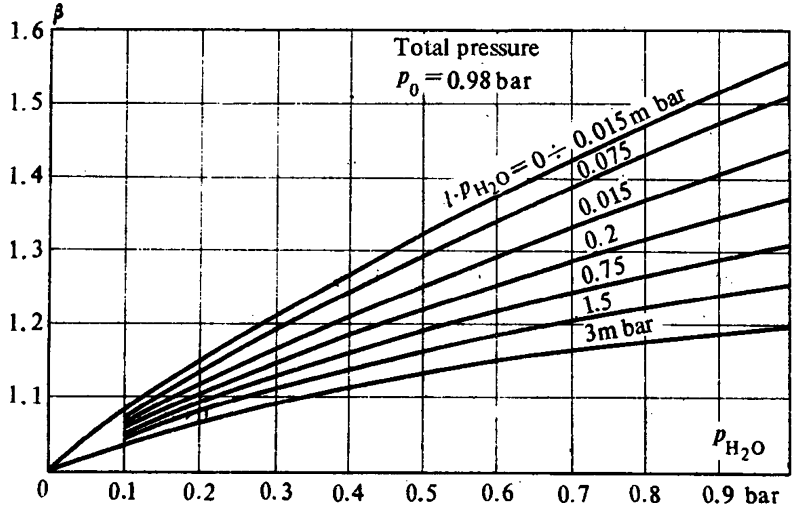


FIG. 29-9

The effective thickness of the layer of gas is taken from Table 29-2.

q_{rad} is used below to determine the coefficient of heat transfer by thermal radiation in formula (29-26).

29-7. Combined Modes of Heat Transfer

Heat is usually transferred from a body at a higher temperature to a body at a lower temperature through a separating wall. Heat is then transferred simultaneously by all the modes of heat transfer—conduction, convection and thermal radiation that have been studied in detail in the preceding chapters. Heat transfer by all modes is referred to as the *combined mode of heat transfer* (Fig. 29-10).

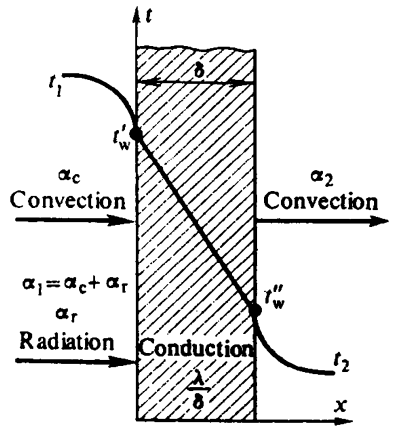


FIG. 29-10

The quantitative characteristic of heat transfer from a gas to a wall (or vice versa) is the total heat-transfer coefficient $\alpha=\alpha_c+\alpha_{rad}$, where α_c accounts for heat transfer by convection and conduction and α_{rad} accounts for heat transfer by thermal radiation.

When designing heat apparatus the rate of heat is calculated by the equation

$$q=\alpha(t_g-t_w) \qquad (29\text{-}28)$$

where α is the total heat-transfer coefficient in the equation for the overall heat-transfer coefficient k.

In this case the overall heat-transfer coefficient for a plane wall becomes

$$k=\frac{1}{\frac{1}{\alpha_1}+\frac{\delta}{\lambda}+\frac{1}{\alpha_2}}=\frac{1}{\frac{1}{\alpha_{c1}+\alpha_{r1}}+\sum\frac{\delta}{\lambda}+\frac{1}{\alpha_{c2}+\alpha_{r2}}}$$

Below the symbols α_1 and α_2 denote the total heat-transfer coefficient accounting for convection, conduction and radiation.

29-8. Thermal-Radiation Heat Transfer in Boiler Furnaces

The burning of fuel in furnaces is accompanied by the formation of high-temperature gases capable of transferring great quantities of heat by radiation. So heat transfer by radiation in the furnaces of modern boilers is of great importance. The total amount of heat transferred to the walls of boiler tubes by radiation can reach 50 per cent or more of the total heat released by fuel combustion. With respect to intensity, radiation heat transfer in furnaces is many times greater than convective heat transfer at medium gas velocities.

The process of outgoing radiation and convective heat transfer proceeds simultaneously with fuel combustion. This considerably complicates research and design calculations for furnaces.

Soviet heat engineers have developed methods of calculating heat transfer in boiler furnaces, based on extensive experimental data, and have suggested practical methods for furnaces using empirical formulae (V. N. Timofeev, A. M. Gurvitch, et al). Furnace calculations usually involve the determination of flue gas temperature at the exit from the boiler furnace. In 1949, in the Power Institute of the USSR Academy of Sciences, prof. G. L. Polyak and S. N. Shorin suggested a comparatively simple calculation formula for this temperature

$$\varepsilon K_f(\theta_1^4-\theta_2^4)+\theta_1-1=0,$$

where $\theta_1 = \frac{T_1}{T_g}$ = dimensionless temperature of flue gases at the furnace exit;

T_1 = temperature of flue gases at the furnace exit, K;

T_g = theoretical combustion temperature for the fuel, K;

$\theta_2 = \frac{T_2}{T_1}$ = dimensionless temperature of boiler wall;

T_2 = temperature of furnace walls, K;

ε = fictitious furnace chamber emissivity, taking into account the peculiarities involved in radiation heat transfer from a moving, burning, emitting medium, the averaging of temperature and the convective heat exchange with the walls;

$$K_f=\frac{5.77\times10^{-8}F_rT_g}{BV_gc'_{c.p}},$$ furnace criterion,

where F_r = radiation heat-transfer surface area of furnace walls;

B = hourly fuel consumption;

V_g = quantity of combustion products obtained, m³/kg;

$c'_{c\,p}$ = mean volumetric heat capacity of products of combustion in the temperature interval T_g-T_1.

With the furnace criterion K_f ranging from 0 to 2 for many industrial furnaces ε can be assumed to be approximately equal to 0.85.

The emissivity ε must reflect the shape of the furnace, the method of fuel combustion in the furnace, the peculiarities of the arrangement of the emitting surfaces and the nature of flue gas flow.

More detailed data on furnace calculation can be found in "Heat Calculations for Boiler Units" [Teplovoi raschet kotelnykh agregatov (normativnii metod), M., Gosenergoizdat, 1957].

Typical Questions and Examples to Chapter Twenty Nine

1. What is the nature of radiant energy?
2. How are rays distinguished from one another?
3. Give the classification of electromagnetic oscillations.

4. Into what parts is radiant energy divided?
5. What is meant by absorptivity, reflectivity and transmissivity?
6. What are meant by an absolutely white surface, an absolutely black, an absolutely transparent, a diffuse and a spectral (mirror) surface?
7. What are the radiation spectra of solids, liquids and gases?
8. What is the emissive ability of a body called?
9. What is meant by the term radiation intensity?
10. What is the basic law of absorption?
11. State Planck's law and give its graphical representation.
12. State the Wien law of displacement.
13. The Stefan-Boltzmann law.
14. Emission coefficient of an absolutely black body.
15. Discuss grey bodies. What is meant by emissivity?
16. State the Kirchhoff law of radiation.
17. Discuss the analysis of the equation of the Kirchhoff law of radiation.
18. Discuss radiation heat transfer between parallel surfaces.
19. State the Lambert cosine law. For what bodies is the law valid?
20. Discuss radiation heat transfer between bodies, where one is situated inside the other.
21. Discuss the equation of radiation heat transfer between bodies arbitrarily arranged in space.
22. What is the effect of screens?
23. What gases emit radiation?
24. Discuss the absorption coefficient of gases.
25. How are the mean temperature of a gas, its partial pressure and the mean beam length determined?
26. Discuss the Schack calculation of radiation from gases.
27. Discuss the determination of the total radiation heat flux and of the coefficient of heat transfer by radiation.
28. What is meant by the combined mode of heat transfer?
29. How is the total heat-transfer coefficient determined?
30. Discuss radiation heat transfer in furnaces.

Example 29-1. Determine the radiation heat transfer between two large parallel surfaces at temperatures $T_1=800$ K and $T_2=400$ K. The emission coefficient of the first surface is $C_1=5.1$ and of the second—$C_2=4.2$ W/m^2·K^4.

The loss of heat from the side surfaces may be ignored. How shall the rate of radiation heat transfer change if, under the same conditions, the emission coefficient of the second surface is $C_2=0.4$ W/m^2·K^4?

The rate of radiation heat transfer between parallel surfaces is determined by Eq. (29-12)

$$q=\frac{1}{\frac{1}{C_1}+\frac{1}{C_2}-\frac{1}{C_s}}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]=\frac{1}{\frac{1}{5.1}+\frac{1}{4.2}-\frac{1}{5.77}}\left[\left(\frac{800}{100}\right)^4-\left(\frac{400}{100}\right)^4\right]=$$

$$=15\,000 \text{ W/m}^2.$$

The rate of radiation heat transfer between parallel surfaces under the condition that $C_2=0.4$ W/m²·K⁴ is equal to

$$q=\frac{1}{\frac{1}{5.1}+\frac{1}{0.4}-\frac{1}{5.77}}\left[\left(\frac{800}{100}\right)^4-\left(\frac{400}{100}\right)^4\right]=1540 \text{ W/m}^2.$$

The calculation indicates that the replacement of one of the surfaces with a polished material caused a reduction of the rate of heat transfer by almost ten times.

Example 29-2. A non-insulated cylindrical steel heater is installed in a workshop. The surface of the heater is heavily oxidized and its emission coefficient is $C_1=5.2$ W/m²·K⁴; the temperature of the outside surface $T_1=430$ K; the length of the heater $l=2$ m, its diameter $d=1$ m; room temperature $T_2=300$ K and the emission coefficient of the walls $C_2=3.5$ W/m²·K⁴; the room is 10 m long, 8 m wide and 4 m high.

Determine the quantity of heat exchange by radiation between the surfaces of the heater and walls of the room.

The quantity of heat transferred by radiation between surfaces is determined by Eq. (29-14)

$$Q=\frac{1}{\frac{1}{C_1}+\frac{F_1}{F_2}\left(\frac{1}{C_2}-\frac{1}{C_s}\right)}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]F_1.$$

The surface area of the heater

$$F_1=3.14\times1\times2+\frac{2\times3.14}{4}=7.85 \text{ m}^2.$$

The surface area of room walls $F_2=304$ m².

$$Q=\frac{1}{\frac{1}{5.2}+\frac{7.85}{304}\left(\frac{1}{3.5}-\frac{1}{C_s}\right)}\left[\left(\frac{430}{100}\right)^4-\left(\frac{300}{100}\right)^4\right]7.85=10\,500 \text{ W}.$$

The ratio $\frac{F_1}{F_2}=0.256$ is small, therefore, assuming $\frac{F_1}{F_2}=0$, then

$$Q=5.2\left[\left(\frac{430}{100}\right)^4-\left(\frac{300}{100}\right)^4\right]7.85=10\,640 \text{ W}.$$

The calculation shows that when the ratio $\frac{F_1}{F_2}$ is small the intensity of radiation heat transfer can be determined by the emission coefficient of the internal body only.

Example 29-3. A screen is placed between two surfaces whose emission coefficients are equal to $C_1=C_2=4.8$ W/m²·K⁴, and whose surface temperatures are $T_1=600$ K, $T_2=300$ K.

Determine the rate of radiation heat transfer between the surfaces before and after the screen has been put into position, and also the screen temperature, if $C_{sc}=C_1=C_2$.

Before the screen was placed the rate of radiation heat transfer between the surfaces

$$q=\frac{1}{\frac{1}{C_1}+\frac{1}{C_2}-\frac{1}{C_s}}\left[\left(\frac{T_1}{100}\right)^4-\left(\frac{T_2}{100}\right)^4\right]=\frac{1}{\frac{1}{4.8}+\frac{1}{4.8}-\frac{1}{5.77}}\times\left[\left(\frac{600}{400}\right)^4-\left(\frac{300}{100}\right)^4\right]=$$

$$=5070 \text{ W/m}^2,$$

and after the screen has been placed

$$q_1=0.5q=0.5\times 5070=2535 \text{ W/m}^2.$$

The temperature of the screen is determined from equation

$$\left(\frac{T_{sc}}{100}\right)^4=\frac{1}{2}\left[\left(\frac{T_1}{100}\right)^4+\left(\frac{T_2}{100}\right)^4\right]=\frac{1}{2}\left[\left(\frac{600}{100}\right)^4+\left(\frac{300}{100}\right)^4\right]=690,$$

whence

$$T_{sc}=512 \text{ K}.$$

Example 29-4. By how many times shall the rate of heat transfer by radiation between two surfaces be reduced, if their emission coefficients are $C_1=C_2=5.2$ W/m^2·K^4 and if a nickel screen is placed between them with an emission coefficient $C_{sc}=0.4$ W/m^2·K^4?

The reduced emission coefficient for the surfaces is equal to

$$C_{red}=\frac{1}{\frac{1}{C_1}+\frac{1}{C_2}-\frac{1}{C_s}}=\frac{1}{\frac{1}{5.2}+\frac{1}{5.2}-\frac{1}{5.77}}=4.76 \text{ W/m}^2\cdot\text{K}^4.$$

The reduced emission coefficient for a surface and screen

$$C'_{red}=\frac{1}{\frac{1}{5.2}+\frac{1}{0.4}-\frac{1}{5.77}}=0.472 \text{ W/m}^2\cdot\text{K}^4.$$

Comparing the equations of radiation heat transfer between two surfaces with and without a screen, we obtain formula (29-20):

$$q_1=0.5\left(\frac{C'_{red}}{C_{red}}\right)q_0=0.5\left(\frac{0.472}{4.76}\right)q_0=0.0496q_0.$$

It follows from this that one screen made from polished nickel reduces the rate of radiation heat transfer 20 times, to an amount equal to only 4.96 per cent of the amount of heat transferred by radiation between the two surfaces without a screen.

Example 29-5. Flue gases contain 15 per cent carbon dioxide and 10 per cent water vapour. The temperature of the gas at the inlet to a channel is $T'_g = 1400$ K, and at the outlet from the channel, $T''_g = 1100$ K; the surface temperature of the flue at the gas inlet is $T'_w = 900$ K, and at the outlet is $T''_w = 700$ K. The emissivity of the flue surface is at $\varepsilon_w = 0.85$. The pressure of the flue gases is 1 bar.

Determine the amount of heat transferred by thermal radiation from the gases to 1 m² of the surface of a cylindrical flue having a diameter $d = 1$ m. Also determine the radiation heat-transfer coefficient.

The mean wall temperature is determined by Eq. (29-21)

$$T_w = \frac{T'_w + T''_w}{2} = \frac{900 + 700}{2} = 800 \text{ K}.$$

The mean temperature of the flue gases is calculated by formula (29-22)

$$T_g = T_w + \frac{(T'_g - T'_w) - (T''_g - T''_w)}{2.3 \log (T'_g - T'_w)/(T''_g - T''_w)} = 800 + \frac{(1400 - 900) - (1100 - 700)}{2.3 \log \frac{500}{400}} =$$

$$= 1250 \text{ K}.$$

The mean beam length for an infinite cylinder is determined from Table 29-2

$$l = 0.9d = 0.9 \times 1 = 0.9 \text{ m}.$$

The amount of heat transferred to the walls of the channel is determined from Eq. (29-27)

$$q_{rad} = \varepsilon'_w C_s \left[\varepsilon_g \left(\frac{T_g}{100} \right)^4 - \varepsilon'_g \left(\frac{T_w}{100} \right)^4 \right].$$

The products of the mean beam length and the partial pressure of carbon dioxide and water vapour are equal to

$$p_{CO_2} l = 0.15 \times 0.9 = 0.135 \text{ m·bar};$$

$$p_{H_2O} l = 0.1 \times 0.9 = 0.09 \text{ m·bar}.$$

Using the values found and the mean gas temperature, we find from the charts in Figs. 29-7 to 29-9 the emissivity of carbon dioxide (CO_2) and water vapour (H_2O)

$$\varepsilon_{CO_2} = 0.098; \quad \beta\varepsilon_{H_2O} = 1.04 \times 0.096 = 0.1.$$

In the same manner we find the emissivity of the gases at the mean surface temperature of the flue

$$\varepsilon'_{CO_2} = 0.1250; \quad \beta\varepsilon'_{H_2O} = 1.04 \times 0.125 = 0.130.$$

The emissivity of the flue gases at the mean gas temperature

$$\varepsilon_g = \varepsilon_{CO_2} + \beta\varepsilon_{H_2O} = 0.0980 + 0.1 = 0.198.$$

The absorptivity of the gas at the mean surface temperature of the flue amounts to:

$$\varepsilon'_g=\varepsilon'_{CO_2}+\beta\varepsilon'_{H_2O}=0.1250+0.130=0.2550.$$

The effective emissivity of the channel walls

$$\varepsilon'_w=\frac{\varepsilon_w+1}{2}=\frac{0.85+1}{2}=0.925.$$

The rate of radiation heat transfer

$$q_{rad}=0.925\times5.77\left[0.198\left(\frac{1250}{100}\right)^4-0.2550\left(\frac{800}{100}\right)^4\right]=20\,220\ \text{W/m}^2.$$

The radiation heat-transfer coefficient is equal to

$$\alpha_{rad}=\frac{q_{rad}}{T_g-T_w}=\frac{20\,220}{1250-800}=44.9\ \text{W/m}^2\cdot\text{deg}.$$

A simpler method for calculation of thermal radiation heat transfer has been developed by A. Schack, Eqs. (29-23) and (29-24).

At the mean gas temperature the quantity of heat radiated from carbon dioxide is

$$q_{CO_2}=4.07\sqrt[3]{pl}\left(\frac{T_g}{100}\right)^{3.5}=4.07\sqrt[3]{0.15\times0.9}\left(\frac{1250}{100}\right)^{3.5}=14\,420\ \text{W/m}^2.$$

At the mean gas temperature the radiation from water vapour

$$q_{H_2O}=40.7p^{0.8}l^{0.6}\left(\frac{T_g}{100}\right)^3=40.7\times0.15\times0.9\left(\frac{1250}{100}\right)^3=11\,880\ \text{W/m}^2.$$

At the mean wall temperature the radiant energy absorbed by the flue gas components CO_2 and H_2O amounts to

$$q_{CO_2}=4.07\sqrt[3]{0.15\times0.9}\left(\frac{800}{100}\right)^{3.5}=3020\ \text{W/m}^2;$$

$$q_{H_2O}=40.7\times0.15^{0.8}0.9^{0.6}\left(\frac{800}{100}\right)^9=3100\ \text{W/m}^2.$$

The rate of heat transfer by radiation is determined by Eq. (29-25)

$$q_{rad}=q_g-q_w=26\,300-6120=20\,180\ \text{W/m}^2.$$

The radiation heat-transfer coefficient is equal to

$$\alpha_{rad}=\frac{20\,180}{450}=44.85\ \text{W/m}^2\cdot\text{deg}.$$

Example 29-6. Determine the temperature of flue gases at the exit from a boiler furnace, assuming: the amount of fuel burnt is $B=2000$ kg/h; the quantity of combustion products per 1 kg of burnt fuel is $V_g=6$ m^3/s; of fuel combustion is $T_g=2000$ K; the mean heat capacity of combustion

products, $C'_{c\,p}=1740$ J/m³·deg. The radiation heat-transfer surface of the boiler $F_r=10$ m².

$$K_f=\frac{5.67\times10^{-8}\times10\times2000^3\times3600}{2000\times6\times1740}=0.78.$$

The emission coefficient of the furnace is assumed equal to $\varepsilon=0.85$. Solving the equation

$$0.85\times0.78\times\theta_1^4+\theta-1=0,$$

we find $\theta_1=0.769$.

That is why the temperature of the flue gases at the exit from the boiler furnace can be determined from the ratio $\theta=\frac{T_1}{T_g}$, whence $T_1=1540$ K.

CHAPTER THIRTY

HEAT-EXCHANGE EQUIPMENT

30-1. Types of Heat Exchangers

Any device (or apparatus) in which one fluid, a hot fluid, transfers heat to a cold fluid is said to be a *heat exchanger*. A variety of liquid and gases are used as fluids in heat exchangers over a wide range of pressures and temperatures. Heat exchangers are classified as *regenerators, direct-contact apparatus* or *recuperators* according to their principle of operation.

In regenerators the hot fluid transfers its heat to an accumulating device which in turn transfers heat periodically to the cold fluid, i.e. in heat exchangers of this type the same heating surface is alternately exposed first to the hot fluid then to the cold one.

In direct-contact apparatus heat is transferred from the hot to the cold fluid by direct mixing of the two fluids, for instance in direct-contact, or mixing, condensers.

Regenerators in which heat is transferred from the hot fluid to the cold one through a separating wall have been widely used in all branches of industry. Only heat exchangers of this kind are considered below.

Heat-exchange equipment may be used for many different purposes as steam boilers, condensers, steam superheaters, central heating systems, etc. Heat exchangers differ usually both in shape and size and in the working media used in them. Notwithstanding the great variety of heat exchangers, their design calculations are basically the same.

In heat exchangers the fluids have three basic flow schemes.

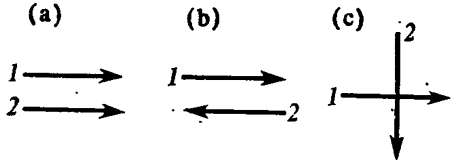


FIG. 30-1

When the primary (hot) and secondary (cold) fluids flow in one direction, parallel to each other, the flow arrangement is referred to as *parallel-flow* (Fig. 30-1*a*). If the two fluid flow parallel to each other, but in opposite directions, the flow arrangement is called *counter-flow* (Fig. 30-1*b*). But if the direction of the hot fluid flow is perpendicular to that of the cold, or secondary, fluid, the pattern of flow is referred to as *cross-flow* (Fig. 30-1*c*).

In addition to these three basic arrangements of fluid flow in heat exchangers, more complicated flow schemes are used, which include all three basic flow arrangements.

30-2. Basic Heat Calculations

When designing new heat-exchange equipment, the purpose of heat calculations is to determine the heat-transfer surface area, and if the latter is known, then the calculations determine the final temperatures of the working fluids. Under steady-state conditions the main heat-transfer equations are the equation of heat transfer by conduction and the heat balance equation.

The equation of heat transfer by conduction (24-6) is

$$Q=kF(t_1-t_2),$$

where Q = heat flux, W;
k = mean overall heat-transfer coefficient, W/m²·deg;
F = heat-transfer surface of exchanger, m²;
t_1 and t_2 = temperatures of the hot and cold fluids respectively.

In the absence of heat losses and changes of phase the heat balance equation is as follows:

$$Q=m_1\Delta i_1=m_2\Delta i_2,$$

or

$$Q=V_1\varrho_1c_{p1}(t_1'-t_1'')=V_2\varrho_2c_{p2}(t_2''-t_2'), \qquad (30\text{-}1)$$

where $V_1\varrho_1$ and $V_2\varrho_2$ = rates of mass fluid flow, kg/s;
c_{p1} and c_{p2} = mean mass heat capacities of the fluids in the temperature interval from t' to t'';
t_1' and t_2' = fluid temperatures at the inlet to the exchanger;
t_1'' and t_2'' = fluid temperatures at the outlet from the exchanger.

The product

$$V\varrho c_p=W$$

is called the *water equivalent.*

With account taken of the above equation the heat balance equation can be presented in the following form:

$$\frac{t_1'-t_1''}{t_2''-t_2'}=\frac{W_2}{W_1}, \qquad (30\text{-}2)$$

where W_2, W_1 are the water equivalents of the hot and cold fluids.

In a heat exchanger the temperatures of the hot and cold fluids are inversely proportional to their water equivalents. This relationship is valid also for each element of the exchanger surface

$$\frac{dt_1}{dt_2}=\frac{W_2}{W_1},$$

where dt_1 and dt_2 represent the temperature changes of the cold and hot fluids over an elementary surface of the exchanger.

The ratio of the water equivalents for the hot (primary) and cold (secondary) fluids determines the slope of the temperature curves on the charts representing temperature change. For instance, if $W_1=2W_2$, then the change in the temperature of the cold fluid will be twice as great as the change in the temperature of the hot fluid.

In deriving the basic equation of conduction (24-6), it was assumed that the temperatures of the hot and cold fluids, or heat-carrying agents, do not change in a heat exchanger. Actually, as the fluids flow through the apparatus their temperatures vary, with the variation in temperature being greatly affected by the fluid flow arrangement and by the magnitude of the water equivalents.

Plotting the values of the surface areas of apparatus along the x-axis and the temperatures at various points on the surface along the y-axis, it is possible to obtain the temperature profiles for a parallel-flow heat exchanger, as shown in Fig. 30-2.

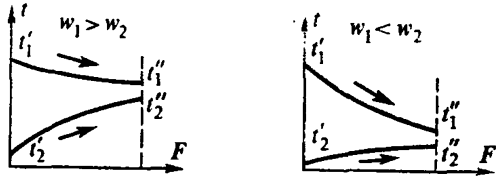


FIG. 30-2

For counter-flow heat exchangers (Fig. 30-3) the upper curves represent the variation in temperature of the hot fluid, and the lower curves—the variation for the cold fluid.

As can be seen from Fig. 30-2 with a parallel-flow arrangement the final temperature of the cold fluid is always lower than the final temperature of the hot fluid. In a counter-flow heat exchanger (Fig. 30-3) the final

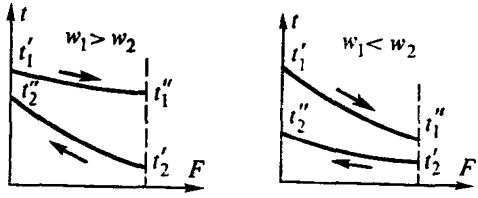


FIG. 30-3

temperature of the cold fluid may be considerably higher than that of the hot fluid. It follows that in counter-flow apparatus it is possible to heat the cold liquid to a higher temperature than in parallel-flow heat exchangers, under otherwise equal initial conditions. In addition, as can be seen from

the illustrations, the variation in temperatures is accompanied by a variation in the difference between the temperatures of the working fluids, i.e. in the temperature difference Δt.

The quantities Δt and k can be assumed to be constant only within the limits of a surface element of the heat-transfer surface, dF. Hence for an elementary heat transfer surface dF the equation of conduction is valid only in differential form

$$dQ=k\,dF\,\Delta t. \tag{30-3}$$

For a constant mean overall heat-transfer coefficient k, the heat flux transferred through the surface F is determined by integrating Eq. (30-3)

$$Q=\int_0^F k\,dF\,\Delta t=kF\,\Delta t_m, \tag{30-4}$$

where Δt_m is the logarithmic mean temperature difference over the entire heat-transfer surface (see Sec. 30-3).

When the overall heat-transfer coefficient varies considerably on individual sections of the heat-transfer surface, it is averaged

$$k_{av}=\frac{F_1k_1+F_2k_2+\ldots+F_nk_n}{F_1+F_2+\ldots+F_n}.$$

Then, with k_{av}=const, Eq. (30-4) takes the form

$$Q=k_{av}\int_0^F \Delta t\,dF, \quad \text{or} \quad Q=k_{av}\,\Delta t_{av}F.$$

30-3. Mean Temperature Difference

If the temperature of the hot and cold fluids varies linearly (Fig. 30-4, dotted lines) the mean temperature difference in a heat exchanger is equal to the arithmetic mean temperature difference

$$\Delta t_m=\frac{t_1'+t_1''}{2}-\frac{t_2'+t_2''}{2}. \tag{30-5}$$

However, the temperatures of the working fluids do not vary linearly, therefore Eq. (30-5) is approximate and it can be applied only when the temperatures of the two fluids vary slightly.

Let us determine the mean temperature difference Δt_m for a parallel-flow heat exchanger in which the variation in fluid temperature is not linear, as shown in Fig. 30-4.

Assume that in the arbitrary section A the temperature of the hot fluid is t' and the temperature of the cold fluid—t''. The difference between the two temperatures

$$t'-t''=\tau. \tag{a}$$

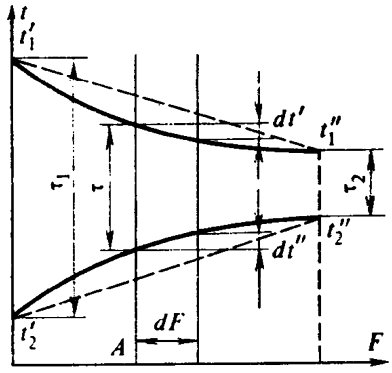


FIG. 30-4

The amount of heat transferred from the hot fluid to the cold one through the elementary heat-transfer surface dF is determined by the following equation:

$$dQ=k\,dF\tau. \qquad \text{(b)}$$

As heat dQ is being transferred, the temperature of the hot fluid decreases by dt', and the temperature of the cold fluid rises by dt'', then

$$dQ=-m_1c_{p1}\,dt'=m_2c_{p2}\,dt'',$$

or

$$dt'=-\frac{dQ}{m_1c_{p1}} \quad \text{and} \quad dt''=\frac{dQ}{m_2c_{p2}}.$$

Differentiating Eq. (a) and substituting into it the values of dt' and dt'', we obtain

$$d\tau=-\frac{dQ}{m_1c_{p1}}-\frac{dQ}{m_2c_{p2}},$$

or

$$dQ=\frac{d\tau}{\dfrac{1}{m_1c_{p1}}+\dfrac{1}{m_2c_{p2}}}$$

Denote the quantity $\left(\dfrac{1}{m_1c_{p1}}+\dfrac{1}{m_2c_{p2}}\right)$ by n, then

$$dQ=-\frac{d\tau}{n}. \qquad \text{(c)}$$

Let us substitute the value of dQ from Eq. (c) into Eq. (b)

$$-\frac{d\tau}{n}=k\,dF\tau,$$

or

$$-\frac{d\tau}{\tau}=k\,dFn. \qquad \text{(d)}$$

If the quantities n and k are constant, then, integrating Eq. (d) between the limits $t'_1-t'_2=\tau_1$ and $t''_1-t''_2=\tau_2$ and from 0 to F, we find that

$$-\int_{\tau_1}^{\tau_2}\frac{d\tau}{\tau}=nk\int_0^F dF,$$

or

$$\ln\frac{\tau_1}{\tau_2}=nkF,$$

whence

$$n=\frac{\ln\frac{\tau_1}{\tau_2}}{kF}. \qquad \text{(e)}$$

Integrating Eq. (c)

$$Q=\frac{\tau_1-\tau_2}{n}$$

and substituting into it the value of n from Eq. (e), we obtain

$$Q=\frac{\tau_1-\tau_2}{\ln\frac{\tau_1}{\tau_2}}kF. \qquad \text{(30-6)}$$

But from Eq. (30-4) the heat flux is equal to

$$Q=kF\Delta t_m,$$

therefore

$$\Delta t_m=\frac{\tau_1-\tau_2}{\ln\frac{\tau_1}{\tau_2}}. \qquad \text{(30-7)}$$

The quantity Δt_m in Eq. (30-7) is called the *logarithmic mean temperature difference.* Here τ_1 is the difference between the temperatures of the working fluids at one end of the heat exchanger, and τ_2—at the opposite end of the apparatus.

For parallel-flow heat exchangers

$$\Delta t_m=\frac{(t_1'-t_2')-(t_1''-t_2'')}{2.3\log\frac{t_1'-t_2'}{t_1''-t_2''}} \qquad \text{(30-8)}$$

The formula for the mean temperature difference of counter-flow heat exchangers is derived similarly

$$\Delta t_m=\frac{(t_1'-t_2'')-(t_1''-t_2')}{2.3\log\frac{(t_1'-t_2'')}{(t_1''-t_2')}}. \qquad \text{(30-9)}$$

Under equal conditions the numerical value of Δt_m for counterflow heat exchangers is always greater than Δt_m for parallel-flow apparatus, so counter-flow heat exchangers are smaller.

Assuming the temperature of each of the working fluids to vary linearly (the dotted-line temperature profile in Fig. 30-4), the arithmetic mean temperature difference will be somewhat greater than the logarithmic mean.

30-4. Calculation of Outlet Temperatures of Hot Fluids

In practical calculation it is sometimes necessary to determine the final, or outlet, temperatures of the working fluids after passage through a heat exchanger. The known quantities are then the heating surface F, the overall heat-transfer coefficient k, the water equivalents W_1 and W_2 and the initial (or inlet) temperatures t_1' and t_2'. It is required to find the outlet temperatures t_1'' and t_2'' and the amount of heat transferred Q.

Parallel-flow arrangement. Assuming the loss of heat from the heat exchanger to the surroundings to be zero, the amount of heat transferred through an elementary area dF of the surface is equal to

$$dQ = W_1(-dt_1); \quad dQ = W_2(+dt_2),$$

whence

$$d(t_1 - t_2) = -dQ\left(\frac{1}{W_1} + \frac{1}{W_2}\right).$$

It is known that

$$dQ = k(t_1 - t_2)\, dF,$$

then

$$\frac{d(t_1 - t_2)}{t_1 - t_2} = -\left(\frac{1}{W_1} + \frac{1}{W_2}\right) k\, dF.$$

Integrating the equation obtained over the entire surface area F, we obtain for parallel-flow heat exchangers

$$\ln \frac{t_1'' - t_2''}{t_1' - t_2'} = -\left(\frac{1}{W_1} + \frac{1}{W_2}\right) kF,$$

or

$$\frac{t_1'' - t_2''}{t_1' - t_2'} = e^{-\left(\frac{1}{W_1} + \frac{1}{W_2}\right) kF}.$$

To determine the outlet temperatures of the working fluids, subtract both sides of the above equation from one

$$1 = \frac{t_1'' - t_2''}{t_1' - t_2'} = 1 - e^{-\left(\frac{1}{W_1} + \frac{1}{W_2}\right) kF},$$

or

$$(t_1' - t_1'') - (t_2' - t_2'') = (t_1' - t_2')\left(1 - e^{-\left(\frac{1}{W_1} + \frac{1}{W_2}\right) kF}\right).$$

It is known from the heat balance equation that

$$t_2'' - t_2' = \frac{W_1}{W_2}(t_1' - t_2''),$$

or

$$t_2' - t_2'' = -\frac{W_1}{W_2}(t_1' - t_1'').$$

Substituting into the above equation the value of $t_2' - t_2''$, we obtain for the hot fluid

$$(t_1' - t_1'') + \frac{W_1}{W_2}(t_1' - t_1'') = (t_1' - t_2')\left[1 - e^{-\left(\frac{1}{W_1}+\frac{1}{W_2}\right)kF}\right],$$

$$t_1' - t_1'' = (t_1' - t_2')\frac{1 - e^{-\left(1+\frac{W_1}{W_2}\right)\frac{kF}{W_1}}}{1+\frac{W_1}{W_2}} = (t_1' - t_2')\psi_{p\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right);$$

for the cold fluid

$$t_2' - t_2'' = (t_1' - t_2')\frac{W_1}{W_2}\psi_{p\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right).$$

The amount of heat transferred is determined from the equation

$$Q = W_1(t_1' - t_1'') = W_1(t_1' - t_2')\psi_{p\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right).$$

The quantity $\psi_{p\text{-}f}$ is found from Table 30-1.

TABLE 30-1

Values of Function ψ_{p-f} for Parallel-Flow Arrangements

$\frac{W_1}{W_2}$ \ $\frac{kF}{W_1}$	$\frac{1}{30}$	$\frac{1}{10}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3	∞
0	0.033	0.1	0.28	0.39	0.63	0.86	0.96	1.00
0.01	0.033	0.1	0.28	0.39	0.63	0.86	0.95	0.99
0.05	0.033	0.1	0.28	0.39	0.62	0.84	0.91	0.95
0.1	0.033	0.1	0.28	0.38	0.61	0.81	0.89	0.91
0.2	0.033	0.1	0.27	0.38	0.58	0.76	0.81	0.83
0.5	0.033	0.1	0.26	0.35	0.52	0.63	0.66	0.67
1.0	0.033	0.09	0.25	0.32	0.43	0.49	0.5	0.5
2.0	0.033	0.09	0.21	0.26	0.32	0.33	0.33	0.33
5.0	0.032	0.08	0.14	0.16	0.17	0.17	0.17	0.17
10.0	0.028	0.06	0.09	0.09	0.09	0.09	0.09	0.09
20.0	0.024	0.04	0.05	0.05	0.05	0.05	0.05	0.05
50.0	0.016	0.02	0.02	0.02	0.02	0.02	0.02	0.02
100.0	0.009	0.01	0.01	0.01	0.01	0.01	0.01	0.01
∞	0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Counter-flow arrangement. The calculation equations for the final (outlet) temperatures of the working fluids in counter-flow arrangement are derived in the same way as for a parallel-flow arrangement.

The equation for the temperature profile of the hot fluid is

$$t_1' - t_1'' = (t_1' - t_2') \frac{1 - e^{-\left(1-\frac{W_1}{W_2}\right)\frac{kF}{W_1}}}{1 - \frac{W_1}{W_2} e^{-\left(1-\frac{W_1}{W_2}\right)\frac{kF}{W_1}}} = (t_1' - t_2')\psi_{c\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right).$$

The temperature variation of the cold fluid is described by the following equation:

$$t_2' - t_2'' = (t_1' - t_2')\frac{W_1}{W_2}\psi_{c\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right).$$

The quantity of heat transferred is equal to

$$Q = W_1(t_1' - t_2')\psi_{c\text{-}f}\left(\frac{W_1}{W_2}, \frac{kF}{W_1}\right).$$

The value of the quantity $\psi_{c\text{-}f}$ is determined from Table 30-2.

Cross-flow arrangement. The design calculations for counter-flow heat exchangers are quite complicated. They are based on the work done by Nusselt in 1911. Approximate calculations can be made using equations containing the following known quantities: the heating surface area of the

TABLE 30-2

Values of Function ψ_{c-f} for Counter-flow Arrangements

$\frac{W_1}{W_2}$ \ $\frac{kF}{W_1}$	$\frac{1}{30}$	$\frac{1}{10}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3	∞
0.0	0.033	0.1	0.28	0.39	0.63	0.86	0.95	1.0
0.01	0.033	0.1	0.28	0.39	0.63	0.86	0.95	1.0
0.05	0.033	0.1	0.28	0.39	0.62	0.86	0.94	1.0
0.1	0.033	0.1	0.28	0.38	0.61	0.85	0.94	1.0
0.2	0.033	0.1	0.28	0.38	0.60	0.83	0.93	1.0
0.5	0.033	0.1	0.26	0.36	0.57	0.78	0.89	1.0
1.0	0.033	0.1	0.25	0.34	0.51	0.68	0.77	1.0
2.0	0.033	0.09	0.23	0.29	0.39	0.46	0.49	0.5
5.0	0.032	0.08	0.16	0.18	0.2	0.2	0.2	0.2
10.0	0.028	0.06	0.1	0.1	0.1	0.1	0.1	0.1
20.0	0.024	0.04	0.05	0.05	0.05	0.05	0.05	0.05
50.0	0.016	0.02	0.02	0.02	0.02	0.02	0.02	0.02
100.0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
∞	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

apparatus, F, the overall heat-transfer coefficient k, the water equivalents W_1 and W_2 and the inlet temperatures t_1' and t_2'. The problem is to find the outlet temperatures t_1'' and t_2'' and the quantity of heat Q transferred.

The quantity of heat transferred from the hot fluid will be

$$Q=W_1(t_1'-t_1''),$$

from which the outlet temperature is equal to

$$t_1''=t_1'-\frac{Q}{W_1}.$$

For the cold fluid

$$Q=W_2(t_2''-t_2'),$$

whence

$$t_2''=t_2'+\frac{Q}{W_2}.$$

Assuming that the temperatures of the working fluid vary linearly, then

$$Q=kF\left(\frac{t_1'+t_1''}{2}-\frac{t_2'+t_2''}{2}\right).$$

Replacing t_1'' and t_2'' in the above equations by their values, we obtain

$$Q=kF\left(\frac{t_1'+t_1'-Q/W_1}{2}-\frac{t_2'+t_2'+Q/W_2}{2}\right)=kF\left(t_1'-\frac{Q}{2W_1}-t_2'-\frac{Q}{2W_2}\right),$$

or

$$\frac{Q}{kF}=t_1'-\frac{Q}{2W_1}-t_2'-\frac{Q}{2W_2},$$

whence

$$Q=\frac{t_1'-t_2'}{\frac{1}{kF}+\frac{1}{2W_1}+\frac{1}{2W_2}}.$$

Knowing the quantity of heat Q, it is possible to determine by the previous formulae the final (outlet) temperatures t_1'' and t_2''.

Typical Questions and Examples to Chapter Thirty

1. What is a heat exchanger?
2. How are heat exchangers classified?
3. What fluid flow arrangements are in heat exchangers?
4. Give the basic equation of conduction and the heat balance equation.
5. What quantity is called the water equivalent?
6. How do fluid temperatures and water equivalents vary in heat exchangers?
7. Graph the temperature profiles for working fluids in parallel-flow and counter-flow heat exchangers.

8. How is the overall heat-transfer coefficient obtained?
9. How is the arithmetic mean temperature difference across a heat-exchange apparatus determined?
10. Derive the equation for the logarithmic mean temperature difference.
11. Write down the equations for the logarithmic mean temperature difference in parallel-flow and counter-flow heat exchangers.
12. How are the outlet temperatures of the working fluids in parallel-flow, counter-flow and cross-flow heat exchangers determined?

Example 30-1. Determine the heating surface of a counter-flow, water-to-water heat exchanger, if the inlet temperature of the hot water is $t_1'=97$ °C and its rate of flow $m_1=1$ kg/s. The hot water flows along an internal steel tube having diameters $d_2/d_1=40/37$ mm. The thermal conductivity of the steel tube $\lambda=50$ W/m·deg.

The cold water moves along the annular passage formed between the tubes of the heat exchanger and is heated from temperature $t_2'=17$ °C to $t_2''=47$ °C. The inside diameter of the external tube is 54 mm. The rate of cold water flow is $m_2=1.14$ kg/s.

The loss of heat from the heat exchanger to the surroundings by radiation is to be ignored.

The quantity of heat transferred in the heat exchanger is

$$Q=m_2c_{p2}(t_2''-t_2')=1.14\times4190(47-17)=140\,000 \text{ W}.$$

The outlet temperature of the hot water is

$$t_1''=t_1'-\frac{Q}{m_1c_{p1}}=97-\frac{140\,000}{4190}=63 \text{ °C}.$$

The physical properties of the working fluid, water, at the average temperature, is

$$t_1=\frac{t_1'+t_1''}{2}=\frac{97+63}{2}=80 \text{ °C}.$$

Also the density $\varrho_1=972$ kg/m^3; the kinematic viscosity $\nu_1=0.365\times10^{-6}$ m^2/s; the thermal conductivity $\lambda=0.674$ W/m·deg; thermal diffusivity $a_1=1.66\times10^{-7}$ m^2/s; the Prandtl number $\mathrm{Pr}_1=2.2$.

At the mean temperature of the cold water, equal to

$$t_2=\frac{t_2'+t_2''}{2}=\frac{17+47}{2}=32 \text{ °C},$$

its physical properties are as follows: density $\varrho_2=995$ kg/m^3; kinematic viscosity $\nu_2=0.776\times10^{-6}$ m^2/s; thermal conductivity $\lambda_2=0.62$ W/m·deg; thermal diffusivity $a=1.495\times10^{-7}$ m^2/s; the Prandtl number $\mathrm{Pr}_2=5.2$.

The flow velocities are equal to:

hot water

$$w_1=\frac{4m_1}{\varrho_1\pi d_1^2}=\frac{1}{972\times3.14\times0.037^2}=0.96 \text{ m/s};$$

cold water

$$w_2=\frac{4m_2}{\varrho_2\pi(D^2-d_2^2)}=\frac{4\times1.14}{995\times3.14(0.054^2-0.04^2)}=1.03 \text{ m/s.}$$

The Reynolds number for the hot water

$$\mathrm{Re}_1=\frac{w_1d_1}{\nu_1}=\frac{0.96\times0.037\times10^6}{0.365}=97\,300.$$

The local heat-transfer coefficient is determined from Eq. (27-9)

$$\mathrm{Nu}=0.021\,\mathrm{Re}_1^{0.8}\,\mathrm{Pr}_f^{0.43}\left(\frac{\mathrm{Pr}_{f1}}{\mathrm{Pr}_w}\right)^{0.25}\varepsilon_l;\quad \frac{l}{d}>50,$$

therefore $\varepsilon_l=1$.

The temperature of the wall is assumed to be

$$t_{w1}=0.5(t_1+t_2)=0.5(80+32)=56 \text{ °C.}$$

At the temperature we find from Table XI in the Appendix $\mathrm{Pr}_{w1}=3.2$, then

$$\mathrm{Nu}=0.021\times97\,300^{0.8}\times2.2^{0.43}\left(\frac{2.2}{3.2}\right)^{0.25}=262,$$

and the local coefficient of heat transfer, α_1, from the hot water to the tube wall is equal to

$$\alpha_1=\mathrm{Nu}_1\frac{\lambda_1}{d_1}=\frac{262\times0.674}{0.037}=4770 \text{ W/m}^2\cdot\text{deg.}$$

The Reynolds number for the cold water

$$\mathrm{Re}_2=\frac{w_2d_{eq}}{\nu_2}=\frac{1.03\times0.014\times10^6}{0.776}=18\,600$$

where $d_{eq}=D-d_2=54-40=14$ mm.

We assume that $t_{w2}=t_{w1}$, therefore, $Pr_{w2}=3.2$, then

$$\mathrm{Nu}=0.021\,\mathrm{Re}_2^{0.8}\,\mathrm{Pr}_{2f}^{0.43}\left(\frac{\mathrm{Pr}_f}{\mathrm{Pr}_w}\right)^{0.25}=0.021\times18\,600^{0.8}\times5.2^{0.43}\left(\frac{5.2}{3.2}\right)^{0.25}=121,$$

whence the local coefficient of heat transfer, α_2, from the tube wall to the cold water is equal to

$$\alpha_2=\mathrm{Nu}_2\frac{\lambda_2}{d_{eq}}=\frac{121\times0.62}{0.014}=5360 \text{ W/m}^2\cdot\text{deg.}$$

The overall heat-transfer coefficient of the heat exchanger

$$k_{cyl}=\frac{1}{\frac{1}{\alpha_1d_{in}}+\frac{1}{2\lambda}\ln\frac{d_2}{d_1}+\frac{1}{\alpha_2d_{out}}}=\frac{1}{\frac{1}{4770\times0.037}+\frac{2.3}{2\times50}\ln\frac{40}{37}+\frac{1}{5360\times0.04}}=$$

$$=86.3 \text{ W/m}^2\cdot\text{deg.}$$

The logarithmic mean temperature difference is

$$\Delta t_m = \frac{(t_1' - t_2'') - (t_1'' - t_2')}{2.3 \log \frac{t_1' - t_2''}{t_1'' - t_2'}} = \frac{(97-47)-(63-17)}{2.3 \log \frac{97-47}{63-17}} = 48.4 \text{ °C}.$$

The rate of heat flow per 1 m length of the tube is equal to

$$q_l = k \Delta t_m = 86.3 \times 48.4 = 4170 \text{ W/m}.$$

The length of tube of the heat exchanger

$$l = \frac{Q}{q_l} = \frac{140\,000}{4170} = 33.6 \text{ m},$$

and the heating surface area

$$F = \pi d_1 l = 3.14 \times 0.037 \times 33.6 = 3.9 \text{ m}^2.$$

If the fluids are in parallel flow in the heat exchanger, then the logarithmic mean temperature difference is equal to

$$\Delta t_m = \frac{(97-17)-(63-47)}{2.3 \log \frac{97-17}{63-47}} = 39.7 \text{ °C};$$

the rate of heat flow

$$q_l = 86.3 \times 39.7 = 3440 \text{ W/m};$$

the length of heat-exchanger tube

$$l = \frac{140\,000}{3440} = 40.7 \text{ m},$$

and with a parallel-flow arrangement the heating surface

$$F = 3.14 \times 0.037 \times 40.7 = 4.73 \text{ m}^2,$$

i.e. the heating surface of a parallel-flow heat exchanger is greater than that of a counter-flow apparatus by 21 per cent.

Example 30-2. A heat exchanger is required to cool in 1 hour 0.25 m^3 of a hot working fluid with a density of 1100 kg/m^3 and a heat capacity of 3046 J/kg·deg. The inlet temperature of the fluid is 120 °C. 1 m^3 of water at a temperature of 10 °C is used to cool the hot fluid. The known overall heat-transfer coefficient of the heat exchanger is $k = 35$ $W/m^2 \cdot deg$ and its heating surface area $F = 8$ m^2. Determine the outlet temperatures of the two working fluids and the amount of heat transferred with a parallel-flow arrangement.

First, we determine the numerical values of the water equivalents

$$W_1 = V_1 \varrho_1 c_{p1} = \frac{0.25 \times 1100 \times 3046}{3600} = 233 \text{ W/deg};$$

$$W_2 = V_2 \varrho_2 c_{p2} = \frac{1.0 \times 1.0 \times 4190}{3600} = 1165 \text{ W/deg},$$

$$\frac{W_1}{W_2} = \frac{233}{1165} = \frac{1}{5}; \quad \frac{kF}{W_1} = \frac{35 \times 8}{233} = 1.2.$$

From table 30-1 we find

$$\psi_{p\,f}\left(\frac{1}{5};\ 1.2\right) = 0.62.$$

The temperature of the hot fluid at the outlet from the heat exchanger at $t_1' - t_1'' = (120-10)0.62 = 68$ °C is equal to

$$t_1'' = 120 - 68 = 52 \text{ °C}.$$

The quantity of heat transferred

$$Q = W_1(t_1' - t_1'') = 233(120-52) = 15\,850 \text{ W}.$$

Since $t_2'' - t_2' = \frac{Q}{W_2} = \frac{15\,850}{1165} = 13.6$ °C, the outlet temperature of the cold working fluid is

$$t_2'' = 10 + 13.6 = 23.6 \text{ °C}.$$

Example 30-3. If the heat exchanger of example 30-2 is designed to operate with a counter-flow arrangement, preserving the same heat-transfer conditions, we obtain the following:

$$W_1 = 233 \text{ W/deg}; \quad W_2 = 1165 \text{ W/deg}; \quad \frac{W_1}{W_2} = 0.2; \quad \frac{kF}{W_1} = 1.2.$$

From Table 30-2 we find that the function

$$\psi_{cf}(0.2;\ 1.2) = 0.65.$$

With $t_1' - t_1'' = (120-10)0.65 = 73$ °C the outlet temperature of the hot working fluid is equal to

$$t_1'' = 120 - 73 = 47 \text{ °C}.$$

The quantity of heat transferred in the heat exchanger

$$Q = W_1(t_1' - t_1'') = 233(120-47) = 17\,000 \text{ W}.$$

Since $Q = W_2(t_1'' - t_2'); \ t_2'' - t_2' = \frac{Q}{W_2} = \frac{17\,000}{1165} = 15$ °C

the outlet temperature of the cold fluid is equal to

$$t_2'' = 10 + 15 = 25 \text{ °C}.$$

The use of counter-flow in the heat exchanger makes it possible to transfer 7.5 per cent more heat, than is transferred with the parallel-flow arrangement under the same conditions.

CHAPTER THIRTY ONE

HEAT AND MASS TRANSFER IN MOIST BODIES

31-1. Basic Regularities of Heat and Mass Transfer

Many processes of heat transfer in nature and in engineering are accompanied by processes in which there is transport of the mass of a substance. These processes are widespread in the various techniques used in the processing of materials in many branches of modern production technology.

Many of the materials used in agriculture, the chemical, food, timber, oil-refining and construction industries, as well as in other branches of industry, are colloidal capillary-porous bodies which undergo moistening, heating and cooling in the course of processing. These processes are accompanied not only by the transfer of heat inside the material processed (heat transport), but also, simultaneously, by the transport of the substance of one component* into the other (mass transport), i.e. diffusion takes place.

Therefore, calculations for technological processes must be based on the laws governing the simultaneous transport of heat and mass and for this purpose the study of the rate of heat transfer in the material must be associated with a study of the rate of mass transfer (or transport).

Diffusion means the spontaneous process of penetration of one substance into another towards the determination of an equilibrium distribution of concentrations.

When a distinct boundary (interface) is observed between interacting substances the transport of mass is due to the so-called *molecular diffusion.* The appearance of molecular diffusion is associated with the thermal motion of molecules. In other cases mass transport is due not only to molecular diffusion, but also to the intensive mixing of individual fractions of the interacting substances. Diffusion of this kind is referred to as *molar* (macroscopic).

The passage of mass from one phase into another by way of molecular (microscopic) and molar (macroscopic) diffusion is referred to as *mass transfer.* The process of mass transfer continues till a dynamic equilibrium sets in, in the course of which the number of molecules passing from one substance into the other is equal to the number of molecules passing from the second substance into the first.

The following diffusion processes are used in technological processes: the absorption and adsorption of gases and vapours; desorption of gases from liquids and solid absorbents; the distillation of liquids; the extraction

* *Component* is the name given to any chemically homogeneous substance.

of liguid and solid substances; the crystallization and solution of solid substances; the drying of moist materials.

If component substances of a mixture have different concentration in all directions, then each mixture component moves in the direction of smaller concentration, so that the concentration of the components in the mixture evens out. Diffusion of this kind is referred to as *concentration diffusion.*

Molecular diffusion due to non-uniform temperature distribution is referred to *thermal diffusion.*

The process of diffusion due to non-uniform pressure is called *pressure diffusion.* This takes place when there are considerable pressure drops, but these are rarely encountered in heat-transfer processes.

Under isothermal conditions the intensity, or rate, of concentration diffusion is characterized by the rate of mass flow, which is determined by Fick's law: *the rate of mass flow due to diffusion* (the amount of substance diffusing per unit time through unit area of the concentration surface) *is directly proportional to the concentration gradient.*

When modes of diffusion are involved in the transport of the mass of one component into another, then the flux per unit area or the mass flow rate per unit area G is determined from the equation

$$G=G_{cd}+G_{td}+G_{pd}=-D\left(\frac{\partial \varrho_i}{\partial n}+\varrho\frac{k_t}{T}\frac{\partial T}{\partial n}+\frac{\varrho_1\varrho_2}{\varrho}\frac{\mu_2-\mu_1}{\mu}\frac{\partial p}{\partial n}\right),$$

where $G_{cd}=-D\frac{\partial \varrho_i}{\partial n}$ = mass flow rate due to concentration diffusion [where ϱ_i is the density (concentration) of the given component, equal to the ratio of the mass of this component to the volume of the mixture, (kg/m³); D is the coefficient of mutual molecular diffusion or the coefficient of diffusion depending on the properties of the diffusing component and on the properties of the medium in which the component propagates, m²/s; $\frac{\partial \varrho_i}{\partial n}$ is the concentration gradient, always directed to the side of increasing concentration; n=direction of the normal to the surface of equal concentration of the given substance];

$G_{td}=-D\varrho\frac{k_t}{T}\frac{\partial T}{\partial n}$ = the rate of mass flow due to thermal diffusion;

ϱ = density of the mixture, kg/m³;

ϱ_1, ϱ_2 = the densities of the components;

T = the local mixture temperature, K;

$k_t=D_{td}/D$ = the thermodiffusion ratio (where D_{td}=coefficient of thermal diffusion);

$\frac{\partial T}{\partial n}$ = the temperature gradient;

G_{pd} = the rate of mass flow taking into account pressure diffusion:

$$G_{pd} = -D \frac{\varrho_1 \varrho_2}{\varrho} \frac{\mu_2 - \mu_1}{\mu} \frac{1}{p} \frac{\partial p}{\partial n},$$

where $\frac{\partial p}{\partial n}$ = total pressure gradient;

p = local total mixture pressure (sum of local partial pressures);

μ_1, μ_2 = molar masses of components $\left(\mu = \mu_1 \frac{\varrho_1}{\varrho} + \mu_2 \frac{\varrho_2}{\varrho}\right)$.

As was mentioned above, pressure diffusion occurs only in the presence of considerable pressure drops and is ignored in most of heat and mass transfer processes.

The minus sign in the equation indicates that the substance is being transported to the side of lesser concentration.

Thus, the diffusion mass flux or the total transport of the mass of any component by way of molecular diffusion results from concentration diffusion, thermal diffusion and pressure diffusion.

The phenomenon of thermal diffusion in liquids was discovered by G. Ludwig and Soret in 1856-1870 and is known as the Soret effect. Thermal diffusion in gases was predicted by Champen and D. Enscog in 1911-1917 and substantiated experimentally by Champen and Dutson. The phenomenon of moisture transfer in colloidal capillary-porous bodies induced by a temperature difference (thermal diffusivity of moisture) was first discovered in 1935 by A. V. Lykov.

In a moving medium mass is transferred not only by molecular diffusion, but also by convection. When any volume of a mixture with a density ϱ moves with a velocity w the following mass of the mixture is transferred

$$G_c = \varrho w = \sum \varrho_i w.$$

The total mass flow rate per unit area due to molecular and convective transport is determined from the expression

$$G_i = G_{md\,i} + G_{c\,i}.$$

The total mass flow rate per unit area and its components are vector quantities, therefore it is essential to know not only their absolute values, but also their directions of flow.

The main types of bond between moisture and a substance. In considering the laws governing heat and moisture transfer in colloidal capillary-porous bodies and moist materials, an allowance should be made for the kind of bond existing between the moisture and solid skeleton of the body, since with a change in the nature of this bond the physical properties of the substance and the binding energy of the moisture with the material change and this is important when selecting the method of moisture removal from a material.

At the present time, in accordance with the classification suggested by Academician P. A. Rebinder, the following forms of moisture bond are assumed: the chemical bond, the physico-chemical and the physico-mechanical bonds.

Chemically bound moisture is most strongly retained in a substance and can be removed from it only by intensive heat treatment (calcination, roasting), which usually involves a change in the structure of the material itself. In engineering applications this moisture is usually not removed from materials, so the chemical bond is not considered below.

The physico-chemical bond between moisture and a material involves the following forms: adsorptionally-bound moisture and osmotically-bound moisture (swelling moisture).

The adsorptionally-bound moisture is a liquid which is retained on the surface of particles of a colloidal body. The absorption of adsorptionally bound moisture is accompanied by the release of heat. The removal of adsorption moisture, strongly bound with the body, is associated with a corresponding energy expenditure. When adsorptionally-bound moisture is being removed it first evaporates in the material and then the forming vapour migrates to its surface.

Osmotically-bound moisture (swelling moisture) fills the closed cells of the body structure. This moisture is associated with a rather low binding energy. Osmotically-bound moisture is capable of diffusion inside the body as a liquid through the walls of the cells due to the difference between the concentrations inside and outside the cells.

Moisture characterized by a *physico-mechanical* bond is held in the capillaries. Capillaries are classified as microcapillaries (when the radius is less than 10^{-5} cm) and macrocapillaries (when the radius exceeds 10^{-5} cm). Depending on the heating conditions, capillary moisture may move in a body both as a liquid and as a vapour.

By making use of the main thermodynamic relations, it can be shown that in calculating the moisture material binding energy, there is a single criterion for classifying the kind of bond with the material, the magnitude of the so-called *free energy* of isothermal dehydration. Due to the existing bond between the moisture and the material, the pressure of water vapour on top of the surface of the material diminishes, which results in a reduced free energy of the system.

The decrease in the free energy ΔF at a constant temperature T (or binding energy), expressed in terms of the work L that must be spent to separate 1 kmole of water from the material, can be determined by the formula

$$\Delta F = L = RT \ln \frac{p_s}{p_p} = -RT \ln \varphi,$$

where R = the universal gas constant;
p_s = the pressure of free-water saturated vapour;
p_p = the partial pressure of water vapour on top of the material.

It is clear that $\varphi=\frac{p_p}{p_s}$ is the humidity above the surface of the material. The greater the bond between moisture and material, the smaller is the quantity p_p while, on the contrary, for free water p_p becomes equal to p_s and $\varphi=1$, and the binding energy L becomes zero.

Depending on the prevailing kind of bond between moisture and material, all moist, or damp, materials can be classified into three groups. If the moisture contained in a body is mainly retained by capillary forces, the body is said to be a *capillary-porous* one (e.g. moist quartz sand, charcoal, some building materials). If the osmotic form of bond predominates in a body, it is referred to as a *colloidal* body (gelatin, agar-agar, pressed dough, etc.).

If a body contains osmotically-bound and capillary moisture, it is referred to as a *colloidal capillary-porous* body (e.g. peat, clay, wood, cloth, grain, leather).

31-2. Basic Laws Governing Heat and Mass Transfer in Colloidal Capillary-Porous Bodies

When there is a temperature gradient inside a moist material, the moisture moves in the direction of heat flow, thereby creating a moisture-content gradient in the material.

When there is a moisture-content gradient in a colloidal capillary-porous material moisture moves from places with a higher moisture content to places having a lower moisture content. Moisture moves both as a vapour and as a liquid. The rate of liquid and vapour flow per unit area perpendicular to the direction of flow, and unit time, is proportional to the moisture-content gradient in the colloidal capillary-porous body

$$G_l=-D_l\varrho_0\left(\frac{\partial u}{\partial n}\right);$$

$$G_v=-D_v\varrho_0\left(\frac{\partial u}{\partial n}\right).$$

where G_l, G_v = rates of liquid and vapour flow, kg/m²·s;
D_l, D_v = proportionality factors (diffusion coefficients for liquid and vapour);
ϱ_0 = density of absolutely dry material;
$\left(\frac{\partial u}{\partial n}\right)$ = moisture-content gradient.

The minus sign in the equations indicates that moisture content decreases in the direction of the normal.

If moisture moves both as a vapour and liquid simultaneously, the total moisture flux

$$G_u=G_l+G_v=-D\varrho_0\left(\frac{\partial u}{\partial n}\right), \tag{31-1}$$

where $D=D_l+D_v$ is the coefficient of diffusion for a colloidal capillary-porous body, m²/s. It depends on moisture content and temperature.

The diffusion coefficient D is defined as the sum of four summands, each of which characterizes the flow of a certain kind of moisture

$$D=\frac{D_a\mu_v}{RT\varrho_0}\frac{\partial p}{\partial n}+D_0+D_{cv}+D_{cl},$$

where D_0 = diffusion coefficient characterizing the flow of osmotic moisture;
D_{cv} = diffusion coefficient characterizing the flow of vapourized capillary moisture;
D_{cl} = diffusion coefficient characterizing the flow of capillary moisture;
$\frac{D_a\mu_v}{RT\varrho_0}\frac{\partial p}{\partial u}$ = diffusion coefficient characterizing the flow of adsorption moisture;
μ_v = molar mass of vapour;
R = universal gas constant;
T = absolute temperature;
$\frac{\partial p}{\partial u}$ = ratio accounting for the relation between the vapour pressure p of a colloidal body and its moisture content u.

Relation (31-1) is the general expression of the law governing the flow of moisture in a colloidal capillary-porous body both as a vapour and as a liquid in the presence of a moisture-content gradient.

If there is a temperature difference in a colloidal capillary-porous body, there will be another moisture flow due to the temperature gradient. The mass rate of that flow, G_t, is proportional to the temperature gradient

$$G_t=-D\varrho_0\delta\left(\frac{\partial t}{\partial n}\right), \tag{31-2}$$

where D = coefficient of diffusion for a colloidal capillary-porous body, m^2/s;
δ = thermal diffusivity of moisture, 1/grad;
$\frac{\partial t}{\partial n}$ = temperature gradient, deg/m.

Equation (31-2) is the analytical expression of the law governing the thermal diffusivity of moisture.

If there exist a moisture-content gradient and a temperature gradient inside a moist body, moisture flow shall be induced both by the conductivity and the thermal diffusivity of moisture. For instance, in the event of contact drying the moisture-content gradient and the temperature gradient coincide, so the phenomenon of thermal diffusivity of moisture intensifies the overall moisture conductivity and drying is intensified (Fig. 31-1). In fact, due to the loss of heat to the surroundings by radiation, the surface layers of the material cool and their temperature becomes lower than that inside the material. Such a temperature distribution causes the appearance of a temperature gradient directed inwards from the surface of the material

to the centre. This temperature gradient raises the total moisture conductivity.

The total moisture flux is then equal to the sum of these two fluxes

$$G=G_u+G_t=-D\varrho_0\left(\frac{\partial u}{\partial n}\right)+\left[-D\varrho_0\delta\left(\frac{\partial t}{\partial n}\right)\right]=-D\varrho_0\left[\left(\frac{\partial u}{\partial n}\right)+\delta\left(\frac{\partial t}{\partial n}\right)\right]. \quad (31\text{-}3)$$

Equation (31-3) is the analytical expression of the generalized law governing moisture transfer in colloidal capillary-porous bodies.

If the moisture-content and temperature gradients are oppositely directed, then the direction of the total moisture flux depends on the ratio of the driving forces of moisture conductivity ($\partial u/\partial n$), and thermal diffusivity ($\delta\,\partial t/\partial n$). For instance, in the event of convection drying, due to moisture evaporation and heating of the material from the surface toward the inside (Fig. 31-2), there appear a moisture-content gradient ($\partial u/\partial n$) directed from the surface to the centre of the material and, due to the phenomenon of thermal diffusivity of moisture, there is a moisture-content gradient ($\delta\,\partial t/\partial n$) directed from the centre to the surface of the material. As a result there originate two oppositely directed moisture flows: at the expense of moisture conductivity G_u, directed from the centre to the surface of the material, and due to thermal diffusivity of moisture, G_t, directed from the surface of the material to its centre.

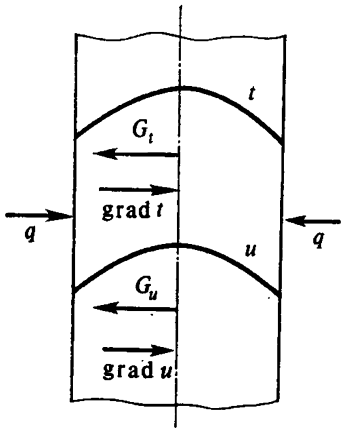


FIG. 31-1

The total moisture flux is determined by equation

$$G=G_u+G_t=-D\varrho_0\left(\frac{\partial u}{\partial n}\right)-\left[-D\varrho_0\delta\left(\frac{\partial t}{\partial n}\right)\right]=$$

$$=-D\varrho_0\left[\left(\frac{\partial u}{\partial n}\right)-\delta\left(\frac{\partial t}{\partial n}\right)\right]. \quad (31\text{-}4)$$

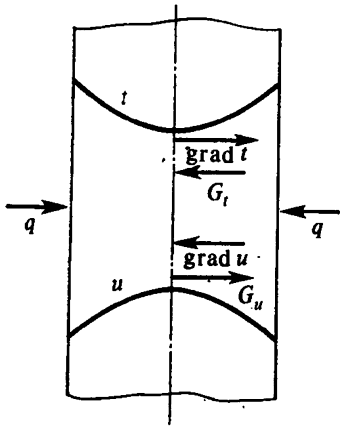


FIG. 31-2

If moisture conductivity is more intensive than the thermal diffusivity of moisture (i.e. the moisture flux caused by moisture conductivity is much greater than the moisture flux due to thermal diffusivity of moisture), then moisture moves in the direction of decreasing moisture content of the material, from the inside layers of the material to its surface, and the thermal diffusivity of moisture interferes with moisture flow.

If the thermal diffusivity of moisture is more intensive than moisture conductivity,

then moisture flows in the direction of heat flow, i.e. in the direction of increasing moisture content, from the surface of the material into it, and moisture conductivity interferes with moisture flow. This phenomenon is observed, for instance, during the beginning of infrared drying or in the course of bread baking: moisture transfer in the direction of heat gradually increases the moisture-content gradient, so that moisture conductivity intensifies and, finally, these driving forces become equal, i.e. the thermal diffusivity of moisture fully balances moisture conductivity. From this moment on the moisture content in the central layers remains constant and drying proceeds at the expense of sinking of the evaporation zone, and there is no moisture flow in the central zones.

The moisture flux caused by thermal diffusivity of moisture also entails additional heat in the direction of the main heat flux. So in the case of heating moist materials, Fourier equation

$$q = -\lambda\left(\frac{\partial t}{\partial n}\right) = ac\varrho\left(\frac{\partial t}{\partial n}\right),$$

which is the main law of heat conduction, reduces to

$$q = -ac\varrho\left(\frac{\partial t}{\partial n}\right) - iG, \tag{31-5}$$

where λ = thermal conductivity;

$\left(\frac{\partial t}{\partial n}\right)$ = temperature gradient;

a = thermal diffusivity, equal to $\frac{\lambda}{c\varrho}$;

c = specific heat capacity;

ϱ = body density;

i = enthalpy of the liquid;

G = rate of moisture flow per unit area.

In Eq. (31-5) the quantity iG represents the amount of heat transported by the moisture.

Applying the main law of moisture flow (31-4) and Fourier's law to moist materials (31-5), we can derive a set of differential equations describing the movement of heat and moisture in moist materials.

The differential equation of mass transport is derived from main transport law, applying the mass conservation law to some arbitrarily taken volume of a body bounded by a closed surface.

The coefficient of diffusion D, the thermal conductivity λ and the thermal diffusivity of moisture δ depend on the moisture content and the temperature. Taking this into consideration, we can obtain a system of non-linear partial differential equations whose solution involves great difficulties. If these quantities are assumed to be constant, then by making use of the mathematical expression of the liquid transport law and the Ostrogradskii-

Gauss transformation, the differential equation of liquid transport can be presented in the following form:

$$\frac{\partial u}{\partial \tau}=D_l\nabla^2 u+D_l\delta_l\nabla^2 t+\varepsilon\left(\frac{\partial u}{\partial \tau}\right), \tag{31-6}$$

where ε is the proportionality factor characterizing the fraction of moisture transported in the form of vapour. This factor is called the *criterion of internal evaporation* (phase change).

If the internal evaporation ($\varepsilon=0$) and inner heat sources, associated with evaporation and condensation are absent then moisture is transported in the form of liquid. If the internal evaporation criterion is equal to unity ($\varepsilon=1$), then the moisture content in the body changes only because of the evaporation of liquid and the condensation of vapour; there is no liquid transport. It follows that the internal evaporation criterion can change from 0 to 1. It is a function of moisture content and temperature, but in a certain temperature and moisture-content interval it can be assumed to be constant.

For the case when the internal evaporation criterion is equal to unity ($\varepsilon=1$) the differential equation for vapour transport remains the same as for liquid transport (provided that the mass-transfer coefficients are identical with the vapour-transfer coefficients)

$$\frac{\partial u}{\partial \tau}=D_v\nabla^2 u+D_v\delta_v\nabla^2 t. \tag{31-7}$$

If calculations are carried out by zones into which a transient process of heat and mass transfer can be divided, then the coefficients D_l and δ_l can be assumed constant for each zone and, in the general case when $\varepsilon<1$, differential equation (31-6) can be given in the following form:

$$\frac{\partial u}{\partial \tau}=D_v\nabla^2 u+D\delta_l\nabla^2 t, \tag{31-8}$$

where

$$D=\frac{D_l}{1-\varepsilon}; \qquad \delta=\delta_l=\delta_v.$$

When applying zonal calculation of heat and mass transfer, the differential equations takes the form:

$$\frac{\partial t}{\partial \tau}=a\nabla^2 t+\varepsilon\left(\frac{r}{\bar{c}}\right)\cdot\left(\frac{\partial u}{\partial \tau}\right); \tag{31-9}$$

$$\frac{\partial u}{\partial \tau}=D\nabla^2 u+D\delta\nabla^2 t. \tag{31-10}$$

where t = body temperature;
u = specific moisture content of the material;
$\bar{c}$ = heat capacity of the moist material: $\bar{c}=c_0+c_m u$, where c_0 and c_m are respectively the heat capacity of dry material and the heat capacity of the moisture contained in it;

r = specific heat of evaporation (of phase change);

$\frac{\partial u}{\partial \tau}$ = change in moisture content in an elementary volume per unit time due to moisture evaporation or vapour condensation inside the material;

∇^2 = Laplacian operator.

The differential equations of heat and mass transfer (31-9) and (31-10) fully describe internal heat and mass transfer. Assuming the mass-transfer characteristics to be constant, solution of these equations makes it possible to calculate the temperature and moisture-content fields for a moist material. The numerical values of the mass-transfer characteristics D, δ, u, $\bar{c}$ of materials at various temperatures and moisture contents are determined experimentally. Several methods are now available for determining mass-transfer characteristics, developed by Soviet and foreign investigators.

31-3. Dimensionless Terms for Heat and Mass Transfer

It is not always possible to obtain a strict analytical solution of differential equations (31-9) and (31-10) for colloidal capillary-porous bodies. However, these differential equations and the conditions of unambiguity permit the use of the theory of similarity to obtain dimensionless terms and criterion equations, which can be used to calculate heat and mass transfer.

The system of differential equations (31-9) and (31-10) and the boundary conditions characterizing the moisture and heat balances on the surface of the material,

$$-D\varrho_0\left(\frac{\partial u}{\partial n}\right)_n - D\varrho_0\delta\left(\frac{\partial t}{\partial n}\right)_n = G; \tag{31-11}$$

$$-\lambda\left(\frac{\partial t}{\partial n}\right)_n + \alpha(t_m - t_s) - r(1-\varepsilon)G = 0 \tag{31-12}$$

(where ϱ_0 is the density of absolutely dry body; t_m is the temperature of surrounding medium; t_s is the surface temperature of the body; G is the mass flow rate), are used to derive a number of dimensionless terms:

the Fourier number

$$\mathrm{Fo} = \frac{a\tau}{l^2}; \quad \mathrm{Fo} = \frac{D\tau}{l^2},$$

characterizing the homochronicity of the heat and mass transfer fields;

the Lykov number

$$\mathrm{Lu} = \frac{D}{a},$$

characterizing the persistence of the moisture-content field compared with that of the temperature field;

the Posnov number

$$\mathrm{Pn}=\frac{\delta \Delta t}{\Delta u},$$

equal to the relative drop in the specific moisture content due to the temperature drop in steady-state conditions;

the Kirpichev number for heat and moisture transfer

$$\mathrm{Ki}=\frac{ql}{\lambda \Delta t}; \quad \mathrm{Ki}_D=\frac{Gl}{D\varrho_0 \Delta u}.$$

The number Ki characterizes the ratio of the heat flux flowing to a body to the heat flux flowing into the body, and Ki_D characterizes the ratio between the rates, or intensities, of external and internal mass transfer;

the Prandtl number for heat flow

$$\mathrm{Pr}=\frac{\nu}{a} \quad \text{and}$$

the Schmidt number for diffusion

$$\mathrm{Sch}=\frac{\nu}{D},$$

allowing for the ratios of velocity, temperature and concentration fields;

the Sherwood number for diffusion

$$\mathrm{Sh}=\frac{\alpha_D l}{D}$$

where α_D is the mass transfer coefficient related to the difference in the concentrations of the diffusing substance, m/s. This coefficient is an analogue of the heat-transfer coefficient.

The Sherwood number characterizes the ratio of the rate of mass transfer and moisture conductivity in the boundary layer;

the Gukhman number

$$\mathrm{Gu}=\frac{T_{db}-T_{wb}}{T_{db}}$$

where T_{db} and T_{wb} are the absolute dry-bulb and wet-bulb temperatures of the gas-vapour mixture.

The Gukhman number characterizes the effect of mass transfer on heat transfer.

The object of experimental investigation of external heat transfer is usually the heat-transfer coefficient α, the Nu number being the unknown or variable dimensionless term and the Fo, Re, Pr, Gr and Gu numbers—the known or reference dimensionless terms. The dimensionless terms are interrelated as follows

$$\mathrm{Nu}=f(\mathrm{Fo}, \mathrm{Re}, \mathrm{Gr}, \mathrm{Pr}, \mathrm{Gu}).$$

In studying mass transfer, treated experimental data are usually presented in the form of the criterion equation

$$\mathrm{Sh}=f(\mathrm{Fo}_D,\ K_1,\ \mathrm{Re},\ \mathrm{Ar},\ \mathrm{Pr}_D',\ \mathrm{Sch},\ \mathrm{Gu}),$$

where the dimensionless term $K_1=\frac{1}{1-\varrho_{10}}$, and ϱ_{10} is determined from equation $\varrho_{10}=\frac{u}{1-u}$ (u is the moisture content).

When applied to individual problems the criterion equations can be simplified. For steady-state processes, for instance, the Fo and Fo_D numbers are omitted; in the event of forced turbulent flow the effect of free convection can be ignored, so the Gr and Ar numbers drop out.

31-4. External Heat and Mass Transfer

The mechanism of heat transfer in the presence of mass transfer differs from that of pure heat transfer. When a liquid evaporates the intensity of external heat and mass transfer is usually determined by the following relationships:

$$q=\alpha(t_g-t_l)=\mathrm{Nu}\left(\frac{\lambda_g}{l}\right)\Delta t; \tag{31-13}$$

$$G=\alpha_D(\varrho_g-\varrho_l), \tag{31-14}$$

where q and G = heat flow rate and mass flow rate per unit area respectively, W/m² and kg/m²·s;

Δt = t_g-t_l = the difference between the temperature of the gas-vapour medium and the surface temperature of a liquid or solid, °C;

ϱ_g and ϱ_l = the vapour density in the surrounding gas-vapour medium and at the surface of a body or liquid, kg/m³;

α and α_D = the heat-transfer and mass-transfer coefficients, W/m²·deg and m/s, respectively;

λ_g = the thermal conductivity of the gas-vapour mixture at the surface of the liquid, W/m·deg;

l = the reference dimension, m.

If the gas component of the gas-vapour mixture is assumed to be an ideal gas, then, using equation $p=\varrho RT$, Eq. (31-14) can be reduced to

$$G=\alpha_D^p(p_g-p_l)=\mathrm{Sh}\frac{\lambda_g D}{l}\Delta p$$

where $\alpha_D^p=\frac{\alpha_D}{RT}$ = the mass-transfer coefficient relative to the difference in partial pressures Δp, $\frac{\mathrm{kg}}{\mathrm{m^2\cdot s\cdot\frac{N}{m^2}}}$ or s/m;

p_g and p_l = partial pressures of vapour in the surrounding gas-vapour medium and at the surface of a body or liquid, N/m²;

λ_{gD} = the diffusivity of the gas-vapour mixture at the liquid surface, $\frac{\text{kg}}{\text{m}\cdot\text{s}\cdot\frac{\text{N}}{\text{m}^2}}$;

Δp = the difference between the partial pressures of vapour in the surrounding gas-vapour medium and at the surface of a solid or liquid, N/m^2.

The Nusselt and Sherwood numbers are determined experimentally by the known rate of heat flow q and the mass flow rate per unit area G, the temperature difference Δt and the partial pressure drop Δp. The quantities λ_g and λ_{gD} are calculated by corresponding formulae or taken from tables.

In conditions of forced convection the Nusselt and Sherwood numbers depend not only on the pattern of flow (Re) and the physical properties of the surrounding medium (Pr and Sch), but also on the thermodynamic properties of the surrounding medium (Gu). The Gukhman thermodynamic evaporation number, Gu, characterizes the accumulating power of the gas-vapour mixture to absorb vapour.

A.V. Nesterenko treated numerous experimental data obtained in studying the evaporation of a liquid from a free surface in adiabatic conditions and forced air convection, and obtained the following empirical formulae:

$$\text{Nu}=k\text{Pr}^{0.33}\text{Re}^{n}\text{Gu}^{m}, \tag{31-15}$$

$$\text{Sh}(\text{Nu}_D)=k'\text{Sch}^{0.33}\text{Re}^{n'}\text{Gu}^{m'} \tag{31-16}$$

where $\text{Pr}=\frac{\nu}{a_g}$ = the Prandtl number;

ν = kinematic viscosity, m^2/s;

a_g = thermal diffusivity of the gas-vapour medium, m^2/s;

$\text{Sch}=\frac{\nu}{D_v}$ = Schmidt number;

D_v = vapour diffusion coefficient, m^2/s.

The values of constants k, n, m, k', n', m' in formulae (31-15) and (31-16), according to Nesterenko, are given in Table 31-1.

TABLE 31-1

Values of Constants in Formulae (31-15) and (31-16)

Reynolds number	k	n	m	k'	n'	m'
$1-2\times10^2$	1.07	0.48	0.175	0.83	0.53	0.135
$3.15\times10^3-2.2\times10^4$	0.51	0.61	0.175	0.49	0.61	0.135
$2.2\times10^4-3.15\times10^5$	0.027	0.9	0.175	0.0248	0.9	0.135

When $Re<200$, the number 2 must be subtracted from Nu in Equation (31-15), i.e. we must write (Nu—2) for Nu. The same must be done for the Sherwood number.

For a liquid evaporating from a free surface in conditions of free convection the heat- and mass-transfer coefficients are calculated by the following formulae suggested by A. V. Nesterenko

$$Nu=5.0(Pr\cdot Ar)^{0.104} \quad \text{for} \quad (Pr\cdot Ar)=3\times 10^6-2\times 10^8; \tag{31-17}$$

$$Sh=0.66(Sch\cdot Ar)^{0.20} \quad \text{for} \quad (Pr\cdot Ar)=3\times 10^6-2\times 10^8. \tag{31-18}$$

When calculating the Nu and Ar numbers the side of a square of an area equal to the surface of the liquid is taken as the reference dimension. The thermal conductivity λ in Eqs. (31-17), (31-18) is calculated by the formula

$$\lambda=\lambda_0+0.0041\varphi,$$

where λ_0 = the thermal conductivity of dry gas;
φ = the gas moisture content.

The diffusion coefficient, or diffusivity, relative to the difference in partial pressures, is calculated by the formula

$$D=D_0\frac{\mu_v T}{RT_0^2}\left(\frac{p_0}{p_v}\right),$$

where D_0 = the diffusion coefficient for a damp gas in standard conditions (for water vapour diffusing into air $D_0=0.079$ m²/s);
μ_v = the mass of 1 kmole of vapour, kg/mole;
p_0 and T_0 = the barometric pressure and temperature in standard conditions ($p_0=101\,325$ N/m², $T_0=273.15$ K);
R = the universal gas constant, J/kmole·deg;
T = the average absolute temperature of the boundary layer:

$$T=273.15+\frac{1}{2}(t_{gv}+t_v);$$

p_p = partial pressure of dry vapour, N/m².

The physical properties of dry air and water may be taken from tables in the Appendix.

When determining heat and mass fluxes associated with external heat and mass transfer it is necessary to calculate the surface temperature, which always differs from the temperature in the bulk of liquid, except in the case of an adiabatic process when it is equal to the air temperature as indicated by a wet-bulb thermometer.

For non-adiabatic conditions the surface temperature can be calculated with sufficient approximation by formulae obtained by A. V. Nesterenko for the evaporation of water from vessels having diameter 210 mm

for free convection

$$\psi = 0.0135\ K^{-1.5}(Ar \cdot Pr)^{0.06};$$

for forced convection

$$\psi = 0.00615\ K^{-0.96}Re^{0.34}.$$

The unknown criterion ψ determined by these formulae is described by the expression

$$\psi = \frac{t_l - t_v}{t_{g\,v} - t_{w\,b}};$$

and the reference criterion

$$K = \frac{t_{g\,v} - t_{w\,b}}{t_l - t_{w\,b}},$$

where t_l = temperature inside the water;
$t_{w\,s}$ = water surface temperature;
$t_{w\,b}$ = wet-bulb thermometer.

The investigations carried out by G. T. Sergeev corroborated the conclusions drawn by A. V. Nesterenko concerning the effect of mass transfer on heat transfer. Sergeev's work widens the field of application of Nesterenko's formulae to $Re = 1.5 \times 10^6$.

G. T. Sergeev conducted a great number of experimental studies devoted to heat and mass transfer upon evaporation of a liquid from the surface of a capillary-porous body, and also to heat transfer for a dry body exposed to turbulent air flow.

The treated test data are represented by the following criterion, or similarity, equations:

for heat transfer

$$Nu = 0.061Re^{0.77}Pr^{0.33}Gu^{0.09};$$

for mass transfer

$$Sh = 0.096Re^{0.75}Sch^{0.33}Gu^{0.144}.$$

In these equations all parameters are related to the temperature of the medium. Tests were conducted with air velocities from 3 m/s to 15 m/s, temperatures—from 25 °C to 90 °C, relative humidities from 5% to 80% and values of the Reynolds number up to $Re = 1.6 \times 10^5$.

An analysis of test results has shown that the intensity, or rate, of heat and mass transfer is directly proportional to the temperature velocity of the air flow, and inversely proportional to the moisture content of the air-vapour mixture.

The investigations fully justified the expediency of introducing the Gukhman number (the spread of test points was reduced considerably) and treating test data by relations such as

$$Nu = f(Re, Pr, Gu)$$

or

$$Sh=f(Re, Sch, Gu),$$

that unambiguously characterize evaporation of liquid both from an open surface and from the surface of a capillary-porous body.

In reality, processes occurring in conditions of free convection only or forced convection only are rarely encountered. For this reason the work conducted by A. V. Nesterenko was extended by L. V. Petrov, who experimentally studied processes of evaporation in conditions of combined free and forced convection.

Compared with the coefficient of heat transfer not involving mass transfer ("dry" heat transfer), the coefficient of heat transfer in a liquid evaporating from a free surface is of great importance. One of the main reasons for the intensification of heat transfer upon evaporation, compared with "dry" heat transfer, is the occurrence of bulk, or volumetric, evaporation. According to the theory of bulk evaporation, as the flow of gas comes into contact with the surface of liquid, non-uniform processes of localized condensation occur along the surface, resulting in the separation of submicroscopic liquid particles which evaporate in the boundary layer. Another reason for the increase of α_{ev} compared with α_{dry} consists in the presence of local evaporation and condensation so that due to an alternating change in the volume of substance (vapour) by a factor 10^3, the structure of the laminar boundary layer is disturbed which intensifies the rate of heat and mass transfer. This phenomenon is most effective when evaporation takes place in a vacuum.

The mechanism of heat and moisture transfer upon evaporation from a moist material (drying) differs essentially from that associated with evaporation from the free surface of a liquid.

Investigations conducted by N. S. Mikheeva have shown that drying proceeds with continuous sinking of the surface of evaporation, resulting in the formation of an evaporation zone whose thickness gradually increases. When evaporation takes place on the surface of a material, then, in adiabatic conditions the surface temperature is constant and equal to the wet-bulb temperature.

As the evaporation surface sinks deeper, the temperature inside the material is lower than its surface temperature. Thus a temperature difference forms in the evaporation zone, increasing from $t_{gv}-t_{sur}$ on the surface of the material to $t_{gv}-t_{wb}$ on the evaporation surface. But an increase in the temperature difference in the direction of heat flow (from the surface inside the material) is accompanied by an increase of the heat-transfer coefficient. Consequently, as the evaporation surface sinks, the heat-transfer coefficient is greater than when evaporation takes place on the external surface of the material; the drop in the intensity of mass transfer (at the end of drying) is then accompanied by a decrease in the rate of heat transfer. From this it follows that mass transfer effects heat transfer.

When moisture evaporates from a damp material and the evaporation surface sinks in the material, vapour is transported through the evaporation zone. Vapour and air molecules move in the micro-capillaries with a high velocity independently from each other, i.e., vapour transfer is not by diffusion, but by effusion.

The effusion mass flow rate is determined by formula

$$G_m = 1.064\psi \sqrt{\frac{\mu_v}{R}} \nabla \left(\frac{p_p}{\sqrt{T}} \right),$$

where μ_v = the molecular mass of vapour;
R = the universal gas constant;
p_p = the partial vapour pressure;
ψ = molecular flow coefficient, proportional to the average capillary radius.

The mass flux (mass flow rate) per unit area is determined from the following equation

$$G_m = -\frac{\mu_v D p}{RT(p - p_p)} \varepsilon \nabla p_p,$$

where p and p_p = barometric and partial vapour pressure respectively;
ε = coefficient characterizing porosity of the material;
∇ = Hamiltonian operator.

The diffusion transport potential is p_p, and the effusion transport potential is $p/\sqrt{T}$. Since the temperature of the evaporation surface, t_m, is lower than the temperature of the external surface of the material, a considerable gradient of effusion transport sets in, giving rise to intensive vapour transfer through the evaporation zone.

If there are in the material capillaries of a radius $r > 10^{-5}$ cm, combined diffusion-effusion vapour transfer through the zone takes place.

The diffusion transport of vapour in the macrocapillaries is hampered by the phenomenon of thermal slippage. If there is a temperature difference along a capillary, circulating air currents appear: at the wall of the capillary they are oppositely directed to the heat flow, while at the axis of the capillary they are in the direction of heat flow. Since at the evaporation surface inside the material the temperature of the capillaries is lower than that at the outer surface, gas is induced to move to the surface of the material. Thus, thermal slippage intensifies vapour transport through the evaporation zone to the surface of the material, i.e., increases the rate of mass transfer.

Heat and mass are transferred from the surface of a material to the surroundings mainly by conduction and diffusion. But the presence of intensive effusion vapour transport in the evaporation zone, boosted by the thermal slippage phenomenon, creates a pressure gradient in the zone. This changes the mechanism of vapour transport in the boundary layer. Vapour leaving the evaporation zone causes the turbulence of the boundary layer of air near the surface of the material, causing a change in the hydro-

dynamic conditions. As a result the mass-transfer intensity increases. Thus, when moisture evaporates from the moist material the intensity of heat and mass transfer is higher than upon liquid evaporation from a free surface.

The main factor effecting heat and mass transfer between a moist capillary-porous material and humid air (processes of drying, evaporative-porous cooling) is the sinking of the evaporation surface which does not occur when liquid evaporates from a free surface.

Sinking of the evaporation surface alters the mechanism of heat and mass transfer both inside the material (internal heat and mass transfer) and outside the material (external heat and mass transfer). That is why heat and mass transfer between the surface of a drying moist material and the surroundings must be regarded as a combination of heat and mass transfer in the evaporation zone inside the material and in the boundary air layer.

31-5. Coefficients of Heat and Mass Transfer

The main transport coefficients are the thermal conductivity, diffusion coefficient, thermal diffusivity and thermal diffusivity of moisture.

In an absolutely dry state heat transfer is not complicated by mass transfer and the thermal conductivities calculated from analytical relationships, are close to the real values.

In an absolutely dry capillary-porous body heat may be transferred by conduction through the solid skeleton of the body, by convection and thermal radiation between the walls of the pores. All these modes of heat transfer are usually determined by the equivalent thermal conductivity λ_e

$$q=\frac{\lambda_e}{l}\Delta t,$$

where q = the rate of heat flow;
Δt = the temperature difference in the pores of the body;
l = the diameter or width of a pore.

The equivalent thermal conductivity is

$$\lambda_e=\lambda_\mu+\lambda_c+\lambda_r,$$

where λ_μ = the molecular thermal conductivity;
λ_c = the convective thermal conductivity, equal to the product of the heat-transfer coefficient α by the characteristic dimension $\lambda_c=\alpha l$ and
λ_r = the radiation thermal conductivity, determined by the ratio

$$\lambda_r=\frac{Q_r l}{\Delta t},$$

where Q_r is the radiation flux.

The thermal conductivities of absolutely dry bodies of equal porosity do not differ significantly from one another.

In moist bodies heat transfer is always accompanied by mass transfer. In the process a mass-transfer gradient arises that depends on temperature, and so the experimental values of thermal conductivities λ represent the equivalent, and not the true values of thermal conductivities.

The thermal conductivity λ is greatly effected by the kind of bond between moisture and material. The thermal conductivity of a damp body depends on temperature and moisture content. Experimental values of the thermal conductivity of damp bodies in the hydroscopic region are indicative of a considerable increase of thermal conductivity with rising temperature, which is explained by the intensification of mass transfer as the temperature increases. The substance is then transferred mainly in the vapour phase.

The difference between the equivalent thermal conductivity λ_e and the true one λ is equal to the supplementary flow of heat induced by mass transfer and related to unit temperature gradient ($\Delta t=1$ deg/m). Consequently, $\lambda_e=\lambda+rD\varrho_0\delta$.

The thermal diffusivity a is equal to the ratio of the thermal conductivity to the total heat capacity of a moist body

$$a=\frac{\lambda}{c_m\varrho_0}$$

where c_m is the specific heat capacity of a moist body, calculated for 1 kg of an absolutely dry body ($c_m=c_0+c_l$, where c_0 and c_l are respectively the specific heat capacities of an absolutely dry body and liquid). Two specific heat capacities of a damp body are distinguished, one calculated for unit mass of an absolutely dry body, c, the other calculated for unit mass of a damp body, c_m.

The two heat capacities c and c_m are related as follows:

$$c_m\varrho=c\varrho_0.$$

The specific heat capacities of absolutely dry bodies do not differ significantly, and for all practical purposes temperature does not affect them.

For most moist bodies thermal diffusivity first increases with increasing moisture content, then diminishes, so that the curve representing thermal diffusivity as a function of moisture content, $a=f(u)$, has a maximum. This maximum corresponds to a change from one kind of bond of the absorbed substance to another.

The thermal diffusivity of moisture δ characterises the relative thermal transfer of vapour and liquid. For most materials δ first increases with increasing moisture content, reaching a maximum value, then diminishes. It depends on the capillary-porous structure of the substance and the mode of mass transfer.

CHAPTER THIRTY TWO

EXPERIMENTAL STUDY OF HEAT TRANSFER

In solving practical heat-transfer problems, difficulties often arise due to the fact that real bodies differ to a great extent from those investigated in the general theory of heat transfer. This difference consists in the heterogeneity of the materials used, variation of their physical properties upon heating, in the detailed shape of real bodies, etc. So when studying heat-transfer processes, experimental work is very important. A knowledge of the main methods applied in studying real bodies experimentally is as necessary as a knowledge of the main laws governing heat transfer. Various types of apparatus used to study heat transfer are treated in detail in special courses. This chapter will give only a brief description of some laboratory work which is of great importance to the study of heat transfer.

32-1. Determination of Thermal Conductivity

Thermal conductivities are determined in steady-state and transient conditions. Only the main methods of determining thermal conductivity that have become widely used are considered below such as the steady-state tube method, the steady-state plate method and the transient method of the regular regime.

Determination of the thermal conductivity of heat-insulation materials by the tube method. The tube method is based on the law governing conduction of heat through a cylindrical wall. The instrument used is schematically shown in Fig. 32-1. A copper tube *2* with an outside diameter d_1 and length *l*

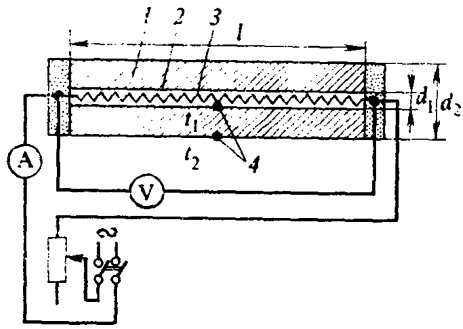


FIG. 32-1

is covered with a cylindrical layer of the material being investigated, with diameter d_2; the tube accommodates electric heater *3* which provides uniform heating. Uniform heating of the insulation *1* is ensured by the good conductivity of the copper tube. Current intensity in the heater is controlled by a rheostat. The heat Q released by heater *3* is determined by the power consumed, measured by an ammeter and a voltmeter. To reduce the heat losses, the ends of the tube are covered with a layer of insulation. The inside and outside surface temperatures of the insulation layer *1*, t_1 and t_2, respectively, are measured with the aid of thermocouples placed in the middle of the tube on the inside and outside surfaces of the insulation. The electromotive force of the thermocouples is measured by means of a laboratory potentiometer.

Under steady-state conditions the entire heat liberated in the heater is transferred to the surrounding medium through the cylindrical wall of the copper tube and the material tested. Measuring the quantity of heat and the inside and outside surface temperatures of the insulation, it is possible to determine the thermal conductivity of the tested material by the following formula:

$$\lambda=\frac{Q\ln\frac{d_2}{d_1}}{2\pi l(t_1-t_2)}=\frac{IE\ln\frac{d_2}{d_1}}{2\pi l(t_1-t_2)}\ \text{W/m·deg},$$

where I = the current intensity in the heater;
E = the potential difference across the heater.

The value of the thermal conductivity calculated by the above formula is related to the average temperature of the material investigated, $t_{av}=0.5\,(t_1+t_2)$.

If there are several values of thermal conductivity determined at different temperatures, thermal conductivity can be plotted as a function of the average temperature of the material tested, $\lambda=f(t_{av})$. For most materials the dependence is linear.

If insulation formed of several layers of different materials tested, then the formula gives the equivalent thermal conductivity of a multilayer insulating wall.

Determination of the thermal conductivity of heat-insulation materials by the plate method. The plate method is based on the law governing heat transfer by conduction through an infinite plane wall. The sectional view of the instrument used to determine thermal conductivity of heat-insulation materials by the plate method is illustrated in Fig. 32-2. The prepared test specimen *1*, a disk with a diameter $D=200$-250 mm and thickness $\delta=5$-30 mm, is clamped between the flat electric heater 2 and cooler 4 that are made from copper. To reduce the loss of heat, additional electric heaters *3* and *5* are fitted underneath and at the sides of the instrument.

Also to reduce the loss of heat to the surroundings, the entire instrument is thoroughly covered with heat-insulation *7* and *8*; screw *9* is used to

tightly clamp the specimen between the cooler and heater. The red copper disks placed between the specimen and the electric heater and also on both sides of insulation *6* serve to even out the surface temperature of the specimen. Temperature is measured with the aid of thermocouples t_1, t_2, t_3, t_4 and t_5. When the system acquires a steady state the heat released in the heater passes completely through the tested material and then to the water flowing through the cooler. The surface temperature of the material tested is measured with thermocouples t_1 and t_2. In order to preclude heat

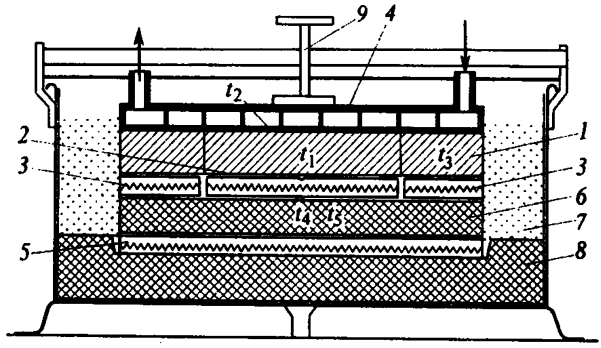


FIG. 32-2

losses in the downward direction, thermocouples t_4 and t_5 must indicate the same temperature. In the absence of radial losses thermocouples t_3 and t_1 must also show the same temperature.

Knowing $Q=IE$, where I=current intensity and E=voltage drop across the central heater, the thermal conductivity of the material tested can be calculated by formula

$$\lambda=\frac{Q\delta}{F(t_1-t_2)}=\frac{IE\delta}{F(t_1-t_2)}\ W,$$

where F = the area of the central heater, m^2;
δ = the specimen thickness, m.

The calculated value of the thermal conductivity is related to the average temperature of the tested material, $t_{av}=0.5(t_1+t_2)$.

If λ is measured at various temperatures, then thermal conductivity can be plotted as a function of the average temperature of the investigated material

$$\lambda=f(t_{av}).$$

32-2. Determination of Thermal Diffusivity of Solids by the Regular-Regime Method

Thermal diffusivity characterizes the ability of a body to change its temperature at a higher or lower rate when heat is added to it. The thermal diffusivity a is determined by the ratio

$$a=\frac{\lambda}{c\varrho}\ \mathrm{m^2/s},$$

where λ = the thermal conductivity;
c = the specific heat capacity of a body;
ϱ = the body density.

Experimental determination of the thermal diffusivity of dry homogeneous bodies is based on Kondratyev's second theorem:

$$a=m_\infty K\ \mathrm{m^2/s}, \tag{32-1}$$

where m_∞ = the rate of body cooling with a local heat-transfer coefficient tending to infinity, $\alpha\to\infty$;
K = the calorimeter shape factor, depending on the dimensions and shape of the body.

The condition $\alpha\to\infty$ can be ensured by placing the tested body into a vigorously stirred liquid. The stirring can be omitted when the test is conducted with the liquid melting or boiling in the thermostat.

The shape factor of a cylinder is determined by formula

$$K=\frac{1}{\left(\frac{2.405}{R}\right)^2+\left(\frac{\pi}{l}\right)^2}\ \mathrm{m^2}, \tag{32-2}$$

where R = cylinder radius;
l = length of cylinder.

For a sphere

$$K=\frac{R^2}{\pi^2}\ \mathrm{m^2}, \tag{32-3}$$

where R is the radius of the sphere.

The radius of a cylindrical calorimeter is determined by formula

$$R=\sqrt{\frac{V}{\pi l}}, \tag{32-4}$$

and the radius of a spherical calorimeter is

$$R=\sqrt[3]{\frac{3}{4}\frac{V}{\pi}}=0.62036\sqrt[3]{V}, \tag{32-5}$$

where V = the volume of the calorimeter (determined by weighing it first empty then filled with water);
l = the length of the cylinder (determined by direct measurement).

The test outfit used to determine thermal diffusivity comprises a water thermostat, cooled calorimeter, drying chamber and measuring instruments.

The arrangement of a water thermostat suitable for temperatures up to 90 °C is schematically shown in Fig. 32-3. The water thermostat *1* is a large-volume cylindrical vessel filled with water and fitted with stirrer *2* driven by an electric motor. The stirrer ensures intensive mixing of the water and a high rate of heat transfer from the surface of the calorimeter to the water. For tests conducted at a temperature above ambient the thermostat is electrically heated. For this purpose the nichrome wire *3* wound around it serves as a heater, and to reduce heat losses, it is covered with good heat insulation *4*. By varying the current intensity through the heater by means of a rheostat, the required water temperature can be maintained. The temperature in the thermostat is maintained constant by means of a thermoregulator and a relay. With higher temperatures (up to 250 °C) oil is used as a thermostatic liquid.

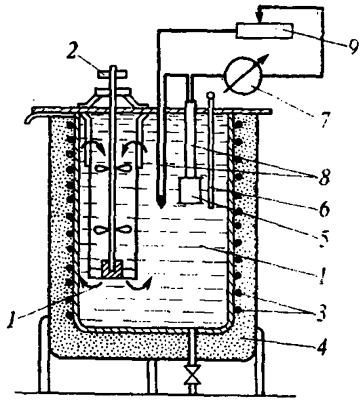


FIG. 32-3

Calorimeter *5* is a metal vessel *1* (Fig. 32-4) filled with the material investigated; one of the junctions of differential thermocouple *2* is arranged in the centre of the vessel. The shape and size of the calorimeter depend on the physical properties of the material handled. Usually, spherical and cylindrical calorimeters are used in practice. Spherical calorimeters, 40 to 80 mm in diameter, are made from steel or red copper; copper cylindrical calorimeters are available from 40 to 60 mm in diameter, 60 to 100 mm high with walls 1 to 2 mm thick.

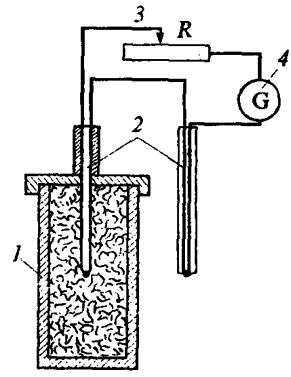


FIG. 32-4

The calorimeter is first warmed up in a drying chamber fitted with an electric heater and a mercury-in-glass thermometer used to measure air temperature inside the cabinet.

The difference between the temperature of the material investigated and the temperature of the liquid in the thermostat is measured with the aid of differential thermocouple *8*. The electromotive force of the thermocouple is measured with the high-sensitivity mirror galvanometer *7* whose sensitivity is varied by connecting to its circuit the decade resistance box *9*.

The temperature of the thermostat liquid is measured with the mercury-in-glass thermometer *6* with a 0.1 °C scale division.

During the test the calorimeter is first placed into a drying chamber in which temperature should exceed that of the thermostat liquid by 5 to 10°. The calorimeter is heated until there is a constant temperature over the entire volume. When this is achieved there is no current flow in the circuit of the differential thermocouple, and the light spot of the galvanometer will be in zero position.

Then the warmed calorimeter is transferred from the drying chamber into the thermostat where it is chilled to full thermal equilibrium with the liquid. During the cooling period galvanometer readings are taken at regular time intervals, read off a stop watch (1-5 min). These characterize the temperature difference $\vartheta = t - t_{av}$. The readings of the thermometer in the thermostat are recorded every 5 to 10 min.

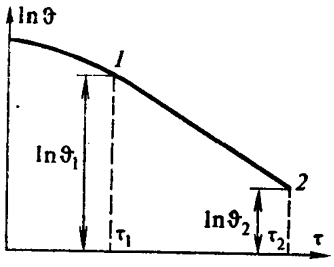


FIG. 32-5

The thermal diffusivity of the material investigated is calculated by formula (32-1). To determine m_∞, the calorimeter cooling data are used to plot a chart $\ln \vartheta = f(\tau)$ (Fig. 32-5): the logarithm of excess temperature ϑ is plotted along the axis of ordinates in scale millimeters, and time in seconds $(\tau_2 - \tau_1)$ is plotted along the x-axis. The graph is usually plotted on logarithmic paper. Then, a straight-line section, characterizing the regular regime of cooling, is selected on the chart. The value of m_∞ is equal to the slope of this straight line. Taking from the chart any two moments of time, τ_1 and τ_2, and their corresponding excess temperatures, the rate of cooling is found from equation

$$m_\infty = \frac{2.3(\log \vartheta_1 - \log \vartheta_2)}{\tau_2 - \tau_1} \frac{1}{s}, \qquad (32\text{-}6)$$

where ϑ_1 and ϑ_2 = excess temperatures, proportional to the deflection angle of the galvanometer spot light;
τ_1 and τ_2 = time intervals corresponding to ϑ_1 and ϑ_2.

The shape factor K is calculated by formula (32-2) or (32-3).

The obtained value of thermal diffusivity a must be taken as relative to the average temperature of the investigated material in the course of cooling

$$t_{av} = \frac{t + t_f}{2},$$

where t = air temperature in the drying chamber;
t_f = temperature of liquid in the thermostat.

If several tests of this kind are conducted at various temperatures, it is possible to plot thermal diffusivity as a function of temperature.

32-3. Determination of the Heat-Transfer Coefficients of Solids by the Regular-Regime Method

To determine thermal conductivity by experiment by the regular-regime method, it is necessary to know the coefficient of heat transfer from the cooled calorimeter to the air in a still-air chamber or in an air thermostat where the air must be at a constant temperature.

The heat-transfer coefficient is determined with the aid of standard, or reference, substances whose well known physical properties change only slightly with temperature, such as red copper, mercury, steel, brass, etc.

The employment of metals with a known heat capacity considerably simplifies the experimental study and permits the use of equation

$$\alpha = m_r \frac{C_r}{F_r} \text{ W/m}^2\cdot\text{deg}, \tag{32-7}$$

where m_r = the rate of cooling of the reference material;
C_r = the total heat capacity of calorimeter, equal to $\varrho_r c_{r\,s}$, i.e. to the product of material density by its specific heat capacity;
F_r = the surface area of calorimeter;
$\frac{C_r}{F_r}$ = the constant of reference calorimeter.

Equation (32-7) is valid from small values of the Biot number which occur in practice for metals with a high thermal conductivity.

The test outfit used to determine the heat-transfer coefficient comprises the thermostat *1*, the cooled reference calorimeter *2*, a drying chamber and required measuring instruments. The layout of the test outfit is shown schematically in Fig. 32-6. The calorimeter is cooled at a constant temperature in the still-air thermostat. The thermostat has a considerable volume and consists of an internal and external cylinders. The space formed between the two cylinders is filled with water which is circulated intensively with the aid of a stirrer driven by an electric motor. This circulating water maintains the wall temperature of the internal cylinder constant. To have the air at the required temperature, the thermostat is fitted with an electric nichrome-wire heater *3*. Constant temperature can be maintained with the aid of a thermoregulator and a relay. The thermostat has a double-walled cover, and its side surface is covered with heat insulation *4*. Air temperature in the thermostat is measured with a mercury-in-glass thermometer *5* with 0.1° scale division.

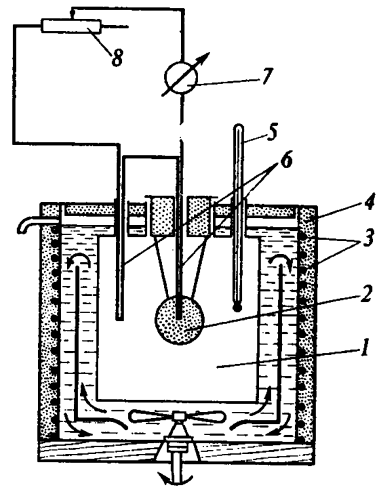


FIG. 32-6

As a calorimeter a metal sphere or cylinder is used which is an exact replica of the surface of the calorimeter holding the test material whose heat-transfer coefficient is to be determined. One junction of differential thermocouple *6* is placed inside the reference calorimeter, and the other junction is kept outside. The electromotive force (emf) of the thermocouple is measured by means of high-sensitivity mirror galvanometer *7* with decade resistance box *8* connected to its circuit. The drying chamber ensures preliminary heating of the reference calorimeter.

The test is conducted as described in Sec. 32-2.

The test data is used to determine the rate of cooling of the reference calorimeter, m_r, from Eq. (32-6). Then the total heat capacity C_r is determined and also the surface area of the calorimeter, F_r.

The heat-transfer coefficient is calculated by Eq. (32-7).

The calculated value of the heat-transfer coefficient must be taken as relative to the average temperature of the calorimeter in the course of cooling

$$t_{av}=0.5(t+t_f),$$

where t = the air temperature in the drying chamber;
t_f = air temperature in the thermostat.

The regular-regime method also permits determination of the thermal conductivity of solids.

32-4. Determination of Heat Losses from Insulated Pipelines and Other Heated Objects

In practice, it is often necessary to check the condition of the insulation of heat apparatus and this involves the determination of rates of heat flow, the equivalent thermal conductivity of insulation and the external and internal surface temperatures of the insulation of the heat apparatus.

It is most important to determine the rate of heat flow. When dealing with cylindrical surfaces the heat flux is determined with the aid of Schmidt's heat meter. The performance of this heat meter is based on the method of the auxiliary wall, in which an auxiliary wall with a known thermal resistance to heat flow is pressed tightly against the object under investigation. But this instrument has a number of shortcomings, since the introduction of the auxiliary wall distorts the temperature field in the layer of insulation.

At the present time a better heat meter of the ИТП-2 type has been developed, free of the shortcomings inherent in Schmidt's heat meter.

The ИТП-2 heat meter is based on the principle of creating a rate of heat flow equal to the rate of heat flow from the surface tested, by means of a special heating element. The rates of heat flow are equalized by making their temperatures the same under otherwise identical conditions of heat transfer.

The heat meter consists of transmitters and a secondary instrument. The transmitters are interchangeable and the secondary instrument is

calibrated by the electrical resistance of the transmitters and their geometrical dimensions. The heat meter permits determination of rates of heat flow up to 580 W/m².

The heat-meter transmitter (Fig. 32-7) consists of the high thermal-conductivity aluminium casing *4* in which are placed heater *3*, made from manganine wire on heat-insulation pad *6*, and a battery of differential thermocouples whose junctions *2* and *5* are located on both sides of the heat-insulation pad. The heater *3* and the junctions of the differential thermocouple *2* are covered with heat conducting copper plate *1* which is the heated element of the heat meter. Thus, the battery of differential thermocouples indicates whether or not there exist a temperature difference between the transmitter casing and the heated element.

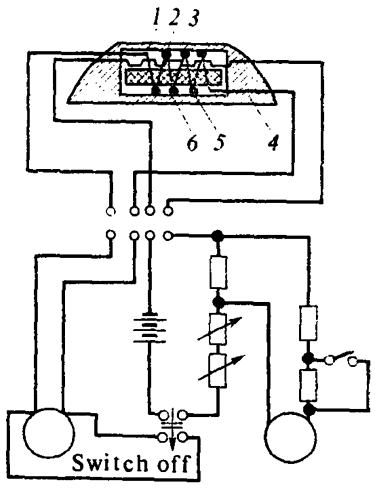


FIG. 32-7

The instrument comprises two transmitters: one is used to measure the rates of heat flow from flat surfaces, and the other, inserted into a rubber plate, is used to measure the rates of heat flow from cylindrical surfaces.

When the transmitter is placed on the heated surface to be tested, the current in the electric heater is adjusted to make the temperature of the transmitter casing equal to the temperature of the heated element. The reading indicating the magnitude of the rate of heat flow is taken after the galvanometer pointer rests in null position for not less than 60 s. To calculate the equivalent termal conductivity of a plain or cylindrical wall, it is necessary to measure, in addition, the temperature t_1 on the inside surface of the insulation and the outside surface temperature t_2.

Then, knowing the rate of heat flow q, we can determine the equivalent thermal conductivity of a plain wall, λ_{eq}, by equation

$$\lambda_{eq}=\frac{q\delta}{t_1-t_2}\ \text{W/m·deg.}$$

The equivalent thermal conductivity of a cylindrical wall is calculated by equation

$$\lambda_{eq}=\frac{q_l \ln\frac{d_2}{d_1}}{2\pi(t_1-t_2)}\ \text{W/m·deg,}$$

where $q_l=\pi d_2 q$=the heat flux for 1 m length of tube, W/m.

The calculated thermal conductivities of the insulation relate to a temperature $t_{av}=0.5(t_1+t_2)$.

32-5. Determination of the Free-Convection Heat-Transfer Coefficient

The schematic layout of the experimental unit is shown in Fig. 32-8. The unit comprises tube 1 having a length $l=1.5$-2.0 m and a diameter $d=40$-60 mm. Arranged inside the tube is the electric heater *3* ensuring uniform lengthwise heating of the tube. To reduce heat losses, the ends of the tube are covered with insulation *2*. The amount of heat generated by the electric heater and transferred from the surface of the tube to the

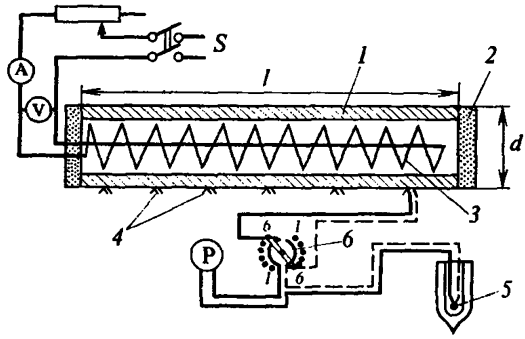


FIG. 32-8

surrounding medium per 1 s (the heat flux) is measured by the power consumed in the heater. The intensity of current flowing through the heater is controlled with a rheostat. The average tube wall temperature is measured with the aid of the hot junctions of thermocouples *4* located at several spirally arranged points. The common cold junction *5*, operated with the aid of selector switch *6*, is placed in a Dewar vessel filled with thawing ice ($t_0=0$ °C).

When the system reaches a steady state all the heat released in the heater is transferred through the tube to the surrounding medium. With natural free convection the heat-transfer coefficient for a horizontal tube is calculated by equation

$$\alpha=\frac{Q_c}{\pi dl(t_w-t_f)} \text{ W/m}^2\cdot\text{deg},$$

where Q_c = the quantity of heat transferred to the air by convection per 1 s;
t_w = the average tube wall temperature;
t_f = the ambient air temperature.

In determining Q_c it should be borne in mind that all the heat Q released by the electric heater is transferred to the surrounding medium not only by convection, but also by thermal radiation, Q_r,

$$Q=Q_c+Q_r; \quad Q_c=Q-Q_r.$$

The heat flux is calculated by the power of the electric heater determined by the ammeter and voltmeter readings

$$Q=IE \text{ W},$$

where I = the current intensity in the heater;
E = the voltage drop through the electric heater.

The quantity of heat lost from the tube to the surrounding medium by thermal radiation per 1 s is determined by equation

$$Q_r=C_{red}\left[\left(\frac{T_w}{100}\right)^4-\left(\frac{T_s}{100}\right)^4\right] F \text{ W},$$

where C_{red} = the reduced coefficient of emission from the tube surface, W/m·K^4;
T_w = the average tube-wall absolute temperature, K;
T_s = the absolute temperature of bodies surrounding the tube (practically equal to the air temperature at a distance from the tube), K;
F = the tube surface area, m^2.

If tests are conducted for various temperature differences, the heat-transfer coefficient α is calculated for different values of Δt and the coefficient is plotted as a function of temperature difference $\alpha=f(\Delta t)$.

For the test results to be applied to other similar processes, they must be generalized on the basis of the theory of similarity and presented as relationships between dimensionless terms. It is well known that for free convection the criterion equation has the following appearance

$$\text{Nu}=f(\text{Gr}, \text{Pr}).$$

The physical properties of air (λ, a, ν) are taken from Table 13 in the Appendix with the average temperature of the boundary layer t_{bl}, equal to $0.5(t_w+t_f)$. The numerical values of the Nusselt, Grashof and Prandtl numbers are determined for each temperature difference and plotted on a logarithmic scale. Then, a straight line is drawn through these points, the equation of this line being

$$\text{Nu}=C(\text{Gr}\cdot\text{Pr})^n.$$

The constant n is determined by the slope of the straight line and the constant C is found from the following ratio for any point on this straight line

$$C=\frac{\text{Nu}}{(\text{Gr}\cdot\text{Pr})^n}$$

The equation obtained is true for similar phenomena in the interval of the measured values of the product (Gr·Pr).

The same method can be applied in studying heat transfer from a vertical tube in conditions of free convection.

32-6. Determination of Emission Coefficients of Grey Bodies

There are three methods of measuring the emission coefficients: the spectra, radiation and calorimetric. Comparing the three methods, the radiation method may be assumed to be the simplest and most exact.

In the general form radiation heat transfer between two surfaces is described by Eq. (29-18). The calculation formula for the radiation method can be obtained allowing for this equation used to determine the amount of energy radiated from a round surface to another round surface, parallelly and coaxially arranged as shown in Fig. 32-9. The equation acquires then the appearance

$$Q = C\frac{\pi}{2}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right](n^2 + A^2 + R^2 - \sqrt{(n^2 + A^2 + R^2)^2 - 4A^2R^2}) \text{ W}, \tag{32-10}$$

where R = the radius of first round surface;
A = the radius of second round surface;
n = the distance between surfaces.

The test outfit used to determine the coefficient of emission of solids (Fig. 32-10)* consists of three main parts: model of a black body *1* with a round hole, sensitive thermal column *3* and heating element for the material investigated.

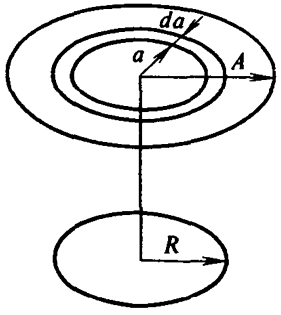


FIG. 32-9

The thermal column *3* comprises a solid copper cylinder with a circular hole of diameter 8 mm in one of its ends. Mounted opposite this hole in the copper cylinder are eighteen manganite-constantan plate thermocouples 0.007 mm thick, covered at the top with platinum black. Placed between the thermal column and the black body and also between the thermal column and the investigated material are water-cooled disks *2* maintained at a constant temperature (t=const).

The heating element for the investigated material is the flat ceramic plate *4* on the surface of which a nichrome spiral is secured. Also secured to this ceramic plate is a thick copper disk *5*. In the several detachable eternit plates *6* secured to the copper disk holes are cut. The investigated material is placed between the eternit plates. The surface temperature of the material investigated must be measured reliably and simply.

The model of the black body, whose emission coefficient, temperature and view factor are known emits radiation upon the round surface of the thermal column. Arranged on the opposite side of the thermal column, between the eternit plates, coaxially with the hole in the blackbody, is the round investigated surface, whose emission coefficient is not known, but

* The instrument has been developed by the author.

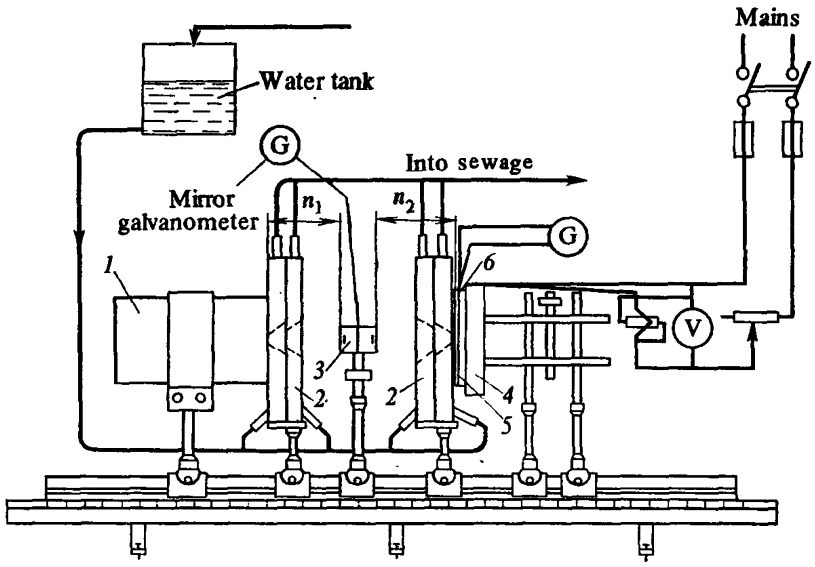


FIG. 32-10

the temperature and view factor are known. The investigated material also emits radiation upon the thermal column. At a definite distance n_1 from the black body to the thermal column and n_2 from the investigated material to the thermal column the deflection of the galvanometer pointer shall be the same, i.e., the quantities of radiant energy shall be the same on both ends of the thermal column. This makes it possible to determine the emission coefficient of the investigated material. Mathematically the radiant energies are related as follows:

$$Q_1 = Q_2 \tag{32-11}$$

[Q_1 and Q_2 are determined from Eq. (32-10)],

$$Q_1 = C_{1n}\frac{\pi}{2}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]\underbrace{(n_1^2 + A^2 + R^2 - \sqrt{(n_1^2 + A^2 + R^2)^2 - 4A^2R^2})}_{\varphi_2} \text{ W},$$

where Q_1 = the radiant energy emitted by the black body surface;
C_{1n} = the reduced emission coefficient;
T_1 = the black surface temperature;
n_1 = the distance from black surface to thermal column;
A = the radius of black surface (hole in the model of black body);
R = the radius of hole in the thermal column.

$$Q_2 = C_{2n}\frac{\pi}{2}\left[\left(\frac{T_3}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]\underbrace{[(n_2^2 + A^2 + R^2)^2 - \sqrt{(n_2^2 + A^2 + R^2)^2 - 4A^2R^2}]}_{\varphi_2} \text{ W},$$

where Q_2 = the radiant energy emitted from investigated material;
C_{2n} = the reduced emission coefficient;
T_2 = the temperature of the investigated material;
n_2 = the distance from investigated material to thermal column.

All other quantities do not change.

As $Q_1 = Q_2$ we obtain

$$C_{1n}\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]\varphi_1 = C_{2n}\left[\left(\frac{T_3}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]\varphi_2.$$

The terms C_{1n} and C_{2n} in above equations are expressed as

$$C_{1n} = \frac{C_1 C'}{C_s}; \quad C_{2n} = \frac{C_2 C'}{C_s},$$

where C_1 = the emission coefficient model of black body *1*;
C' = the emission coefficient of the thermal column;
C_2 = the emission coefficient of the investigated material;
C_s = the emission coefficient of black body.

When the temperatures are the same

$$C_1\varphi_1 = C_2\varphi_2.$$

Analyzing the above equality, it should be noted the emission coefficient of the material investigated is independent of the emission coefficient of the thermal column, which is an advantage of the determination method suggested. As was mentioned above the investigated material is placed on a thick copper disk.

The thermal column, placed on a movable support, is connected to a high-sensitivity mirror galvanometer.

When steady-state conditions set in, i.e., when the surface temperature of the specimen remains unchanged for some time interval (10 min), readings of the mirror galvanometer are recorded as well as the temperature of the investigated material and the distance from the thermal column to the investigated surface. Then the thermal column is turned through 180 °C and moved toward the black body whose temperature is maintained constant during the test. Moving the thermal column on its support, we find its position in which the indication of the mirror galvanometer is the same as from the investigated surface. Then, the distance from the thermal column to the black surface is also measured. The quantities obtained in this way are substituted in Eq. (32-12) in which the unknown is the emission coefficient of the investigated material C_2.

For each temperature of the investigated surface it is necessary to take repeated measurements of the distances both from the investigated material to the thermal column and from the black surface to the thermal column. Test duration is 1-2 hours.

TABLE I

Properties of Saturated Steam (by temperature)

t, °C	$p_н$, bar	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
0	0.006 108	0.001 000 2	206.3	0.004 847	0.000	2500.8	2500.8	0	9.1644
5	0.008 718	0.001 000 1	147.2	0.006 793	21.06	2510.0	2489.0	0.0762	9.0242
10	0.012 271	0.001 000 4	106.42	0.009 398	42.04	2519.2	2477.3	0.1511	8.8995
15	0.017 04	0.001 001 0	77.97	0.012 82	62.97	2528.4	2465.4	0.2244	8.7806
20	0.023 37	0.001 001 8	57.84	0.017 29	83.90	2537.2	2453.4	0.2964	8.6663
25	0.031 67	0.001 003 0	43.40	0.023 04	104.80	2546.4	2441.7	0.3672	8.5570
30	0.042 41	0.001 004 4	32.93	0.030 36	125.69	2555.6	2430.0	0.4367	8.4523
35	0.056 22	0.001 006 0	25.25	0.039 60	146.58	2564.8	2418.3	0.5049	8.3518
40	0.073 75	0.001 007 9	19.55	0.051 15	167.51	2573.6	2406.1	0.5723	8.2560
45	0.095 82	0.001 009 9	15.28	0.065 45	188.41	2582.4	2394.0	0.6385	8.1638
50	0.123 35	0.001 012 1	12.05	0.083 02	209.30	2591.6	2382.3	0.7038	8.0751
55	0.157 41	0.001 014 5	9.578	0.104 4	230.19	2600.4	2370.1	0.7679	7.9901
60	0.199 2	0.001 017 1	7.678	0.130 2	251.12	2609.2	2358.0	0.8311	7.9084
65	0.250 1	0.001 019 9	6.201	0.161 3	272.06	2617.6	2345.4	0.8935	7.8297
70	0.311 6	0.001 022 8	5.045	0.198 2	292.99	2626.4	2333.3	0.9550	7.7544
80	0.473 6	0.001 029 0	3.409	0.293 3	334.94	2643.1	2308.2	1.0752	7.6116
90	0.701 1	0.001 035 9	2.361	0.423 5	376.98	2659.5	2282.5	1.1924	7.4785

TABLE I *(continued)*

t, °C	p_H, bar	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
100	1.013 2	0.001 043 5	1.673	0.597 7	419.10	2675.8	2256.7	1.3071	7.3545
110	1.432 7	0.001 051 5	1.210	0.826 3	416.34	2691.3	2230.0	1.4185	7.2386
120	1.985 4	0.001 060 3	0.891 7	1.122	503.7	2706.3	2202.7	1.5278	7.1289
130	2.701 1	0.001 069 7	0.668 3	1.496	546.4	2720.6	2174.2	1.6345	7.0271
140	3.614	0.001 079 8	0.508 7	1.966	589.1	2734.0	2144.9	1.7392	6.9304
150	4.760	0.001 090 6	0.392 6	2.547	632.2	2746.5	2114.3	1.8418	6.8383
160	6.180	0.001 102 1	0.306 8	3.259	675.3	2757.8	2082.5	1.9427	6.7508
170	7.920	0.001 114 4	0.242 6	4.122	719.3	2768.7	2049.4	2.0419	6.6666
180	10.027	0.001 127 5	0.193 9	5.157	763.3	2778.4	2015.1	2.1395	6.5858
190	12.553	0.001 141 5	0.156 4	6.395	807.6	2786.3	1978.7	2.2358	6.5075
200	15.550	0.001 156 5	0.127 2	7.863	852,4	2793.0	1940.6	2.3308	6.4318
210	19.080	0.001 172 6	0.104 4	9.578	897.6	2798.0	1900.4	2.4246	6.3577
220	23.202	0.001 190 0	0.086 06	11.62	943.7	2801.4	1857.7	2.5179	6.2848
230	27.979	0.001 208 7	0.071 47	13.99	990.2	2803.1	1812.7	2.6101	6.2132
240	33.480	0.001 229 1	0.059 67	16.76	1037.5	2803.1	1765.6	2.7022	6.1425
250	39.78	0.001 251 2	0.050 05	19.98	1086.1	2801.0	1714.9	2.7934	6.0721
260	46.94	0.001 275 5	0.042 15	23.72	1135.0	2796.4	1661.3	2.8851	6.0014
270	55.05	0.001 302 3	0.035 60	28.09	1185.3	2789.7	1604.4	2.9764	5.9298
280	64.19	0.001 332 1	0.030 13	33.19	1236.8	2779.6	1542.8	3.0685	5.8573
290	74.45	0.001 365 5	0.025 53	39.17	1290.0	2766.2	1476.3	3.1610	5.7824
300	85.92	0.001 403 6	0.021 64	46.21	1344.8	2749.1	1404.3	3.2548	5.7049

TABLE I *(concluded)*

t, °C	p_H, bar	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
310	98.69	0.001 447	0.018 31	54.61	1402.2	2727.3	1325.1	3.3507	5.6233
320	112.80	0.001 499	0.015 45	64.74	1462.0	2699.6	1237.6	3.4495	5.5354
330	128.64	0.001 562	0.012 97	77.09	1526.1	2665.7	1139.6	3.5521	5.4412
340	146.08	0.001 639	0.010 78	92.77	1594.8	2621.8	1027.0	3.6605	5.3361
350	165.37	0.001 741	0.008 805	113.6	1671.4	2564.4	893.0	3.7786	5.2117
360	186.74	0.001 894	0.006 943	144.1	1761.4	2481.1	719.7	3.9163	5.0530
370	210.53	0.002 22	0.004 93	202.4	1892.4	2330.8	438.4	4.1135	4.7951
374	220.87	0.002 80	0.003 47	288.0	2031.9	2147.0	114.7	4.3258	4.5029

Critical point parameters:

temperature t_{cr} = 374.12 °C;
pressure p_{cr} = 221.15 bar (22 115 kPa);
specific volume v_{cr} = 0.003 147 m³/kg;
enthalpy i_{cr} = 2095.2 kJ/kg;
entropy s_{cr} = 4.424 kJ/kg·deg.

TABLE II

Properties of Saturated Steam (by pressure)

p, bar	$t_н$ °C	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
0.010	6.936	0.001 000 1	130.04	0.007 690	29.18	2513.4	2484.2	0.1053	8.9749
0.020	17.486	0.001 001 4	67.24	0.014 87	73.40	2533.1	2459.7	0.2603	8.7227
0.025	21.071	0.001 002 1	54.42	0.018 38	88.36	2539.5	2451.1	0.3119	8.6424
0.030	24.078	0.001 002 8	45.77	0.021 85	100.93	2545.3	2444.4	0.3547	8.5784
0.040	29.95	0.001 004 2	34.93	0.028 63	121.33	2553.7	2432.3	0.4225	8.4737
0.05	32.89	0.001 005 4	28.24	0.035 41	137.79	2560.9	2423.1	0.4764	8.3943
0.06	36.17	0.001 006 5	23.77	0.042 08	151.49	2567.1	2415.6	0.5209	8.3297
0.08	41.53	0.001 008 5	18.13	0.055 16	173.89	2576.4	2402.5	0.5919	8.2273
0.10	45.82	0.001 010 2	14.70	0.068 05	191.84	2583.9	2392.1	0.6496	8.1494
0.14	52.57	0.001 013 2	10.69	0.093 53	220.05	2596.1	2376.0	0.7368	8.0305
0.18	57.82	0.001 015 9	8.448	0.118 4	242.03	2605.4	2363.3	0.8040	7.9445
0.20	60.08	0.001 017 1	7.652	0.130 7	251.48	2609.2	2357.7	0.8324	7.9075
0.25	64.99	0.001 019 8	6.201	0.161 3	272.03	2617.6	2345.5	0.8934	7.8300
0.30	69.12	0.001 022 3	5.232	0.191 1	289.30	2624.6	2335.3	0.9441	7.7673
0.4	75.87	0.001 026 4	3.999	0.250 1	317.62	2636.3	2318.7	1.0261	7.6710
0.5	81.33	0.001 029 9	3.243	0.308 3	340.53	2645.2	2304.7	1.0912	7.5923
0.6	85.94	0.001 033 0	2.734	0.365 8	359.90	2653.1	2293.2	1.1453	7.5313
0.8	93.50	0.001 038 5	2.089	0.478 7	391.75	2665.3	2273.5	1.2331	7.4342
1.0	99.62	0.001 043 2	1.696	0.589 6	417.47	2674.9	2257.5	1.3026	7.3579
1.2	104.80	0.001 047 2	1.430	0.699 2	439.34	2683.0	2243.6	1.3610	7.2972

TABLE II *(continued)*

p, bar	t_K, °C	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
1.6	113.31	0.001 054 3	1.092	0.916 0	475.41	2696.3	2220.8	1.4550	7.2017
2.0	120.23	0.001 060 6	0.886 0	1.129	504.74	2706.8	2202.0	1.5306	7.1279
2.6	128.73	0.001 068 4	0.692 9	1.443	541.2	2718.9	2177.7	1.6213	7.0399
3.0	133.54	0.001 073 3	0.605 5	1.652	561.7	2725.5	2163.8	1.6716	6.9922
4.0	143.62	0.001 083 6	0.462 3	2.163	604.3	2738.7	2134.1	1.7766	6.8969
5	151.84	0.001 092 7	0,374 9	2.667	640.1	2748.9	2108.7	1.8605	6.8221
6	158.84	0.001 100 9	0.315 6	3.169	670.6	2756.9	2086.3	1.9311	6.7609
8	170.41	0.001 114 9	0.240 3	4.161	720.9	2769.0	2048.1	2.0461	6.6630
10	179.88	0.001 127 3	0.194 5	5.143	762.4	2777.8	2015.3	2.1383	6.5867
12	187.95	0.001 138 5	0.163 3	6.125	798.4	2784.6	1986.2	2.2156	6.5224
14	195.04	0.001 148 8	0.140 8	7.102	830.0	2789.7	1959.7	2.2841	6.4699
16	201.36	0.001 158 7	0.123 8	8.080	858.3	2793.5	1935.2	2.3437	6.4221
18	207.10	0.001 167 8	0.110 4	9.055	884.2	2796.5	1212.3	2.3975	6.3794
20	212.36	0.001 176 8	0.099 61	10.04	908.6	2799.2	1890.7	2.4471	6.3411
24	221.77	0.001 193 2	0.083 24	12.01	951.8	2801.8	1850.0	2.5346	6.2727
28	230.04	0.001 208 8	0.017 42	14.00	990.2	2803.1	1812.8	2.6101	6.2129
30	233.83	0.001 216 4	0.066 63	15.01	1009.4	2803.1	1794.7	2.6455	6.1859
35	242.54	0.001 234 4	0.057 06	17.53	1049.8	2802.8	1753.0	2.7251	6.1249
40	250.33	0.091 252 0	0.049 77	20.09	1087.5	2800.6	1713.2	2.7965	6.0689
50	263.91	0.001 285 8	0.039 43	25.36	1154.2	2793.9	1639.6	2.9210	5.9739
60	275.56	0.001 318 5	0.032 43	30.84	1213.9	2784.4	1570.5	3.0276	5.8894

TABLE II *(concluded)*

p, bar	$t_н$, °C	v', m³/kg	v'', m³/kg	ϱ, kg/m³	i', kJ/kg	i'', kJ/kg	r, kJ/kg	s', kJ/kg·deg	s'', kJ/kg·deg
70	285.80	0.001 351 0	0.027 38	36.53	1267.6	2772.3	1504.7	3.1221	5.8143
80	294.98	0.001 383 8	0.023 52	42.52	1317.3	2758.6	1441.2	3.2079	5.7448
90	303.31	0.001 417 4	0.020 49	48.80	1363.9	2742.6	1378.8	3.2866	5.6783
100	310.96	0.001 452 2	0.018 03	55.47	1407.9	2724.8	1316.9	3.3601	5.6147
110	318.04	0.001 488 6	0.015 97	62.62	1450.2	2705.2	1255.0	3.4297	5.5528
120	324.64	0.001 527	0.014 26	70.15	1491.1	2684.6	1193.5	3.4966	5.4930
130	330.81	0.001 568	0.012 78	78.22	1531.3	2662.3	1131.1	3.5606	5.4333
140	330.63	0.001 611	0.011 49	87.04	1570.8	2637.9	1067.0	3.6233	5.3731
160	347.32	0.001 710	0.009 319	107.3	1649.6	2581.7	932.1	3.7456	5.2478
180	356.96	0.001 839	0.007 505	133.2	1732.2	2510.6	778.4	3.8708	5.1054
200	365.71	0.002 03	0.005 86	170.5	1826.8	2410.3	583.4	4.0147	4.9280
220	373.7	0.002 73	0.003 67	272.5	2016.0	2168.0	152.0	4.3030	4.5970

TABLE III

Average Molar Heat Capacity of Gases at Constant Pressure μc_{pm}, kJ/kmole·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	29.274	29.019	29.123	35.860	33.499	38.85	29.073
100	29.538	29.048	29.178	38.112	33.741	40.65	29.152
200	29.931	29.132	29.303	40.059	34.118	42.33	29.299
300	30.400	29.287	29.517	41.755	34.575	43.88	29.521
400	30.878	29.500	29.789	43.250	35.090	45.22	29.789
500	31.334	29.764	30.099	44.573	35.630	46.39	30.095
600	31.761	30.044	30.425	45.453	36.195	47.35	40.405
700	32.150	30.341	30.752	46.813	36.789	48.23	30.723
800	32.502	30.635	31.070	47.763	37.392	48.94	31.028
900	32.825	30.924	31.376	48.617	38.008	49.61	31.321
1000	33.118	31.196	31.665	49.392	38.619	50.16	31.598
1100	33.386	31.455	31.937	50.099	39.226	50.66	31.862
1200	33.633	31.707	32.192	50.740	39.825	51.08	32.109
1300	33.863	31.941	32.427	51.322	40.407	—	32.343
1400	34.076	32.163	32.653	51.858	40.976	—	32.575
1500	34.282	32.372	32.858	52.348	41.525	—	32.774
1600	34.474	32.565	33.051	52.800	42.056	—	32.967
1700	34.658	32.749	33.231	53.218	42.576	—	33.151
1800	34.834	32.917	33.402	53.504	43.070	—	33.319
1900	35.006	33.080	33.561	53.959	43.539	—	33.482
2000	35.169	33.231	33.708	54.290	43.995	—	33.641

TABLE IV

Average Molar Heat Capacity of Gases at Constant Volume, μc_{vm}, kJ/kmol·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	20.959	20.704	20.808	27.545	25.184	30.52	20.758
100	21.223	20.733	20.863	29.797	25.426	32.52	20.838
200	21.616	20.800	20.988	31.744	25.803	34.00	20.984
300	22.085	20.972	21.202	33.440	26.260	35.55	21.206
400	22.563	21.185	21.474	34.935	26.775	36.89	21.474
500	23.019	21.449	21.784	36.258	27.315	38.06	21.780
600	23.446	21.729	22.110	37.438	27.880	39.02	22.090
700	23.835	22.027	22.437	38.498	28.474	39.90	22.408
800	24.187	22.320	22.755	39.448	29.077	40.61	22.713
900	24.510	22.609	23.061	40.302	29.693	42.28	23.006

TABLE IV *(concluded)*

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
1000	24.803	22.881	23.350	41.077	30.304	41.83	23.283
1100	25.071	23.140	23.622	41.784	30.911	42.33	23.547
1200	25.318	23.322	23.877	42.425	31.510	42.75	23.794
1300	25.548	23.626	24.112	43.007	32.092	—	24.028
1400	25.761	23.848	24.338	43.543	32.661	—	24.250
1500	25.967	24.057	24.543	44.033	33.210	—	24.459
1600	26.159	24.250	24.736	44.485	33.741	—	24.652
1700	26.343	24.434	24.916	44.903	34.261	—	24.836
1800	26.519	24.602	25.087	45.289	34.755	—	25.004
1900	26.691	24.765	25.246	45.644	35.224	—	25.167
2000	26.854	24.916	25.393	45.975	35.680	—	25.326

TABLE V

Average Mass Heat Capacity of Gases at Constant Pressure, c_{pm}, kJ/kg·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	0.9148	1.0304	1.0396	0.8148	1.8594	0.607	1.0036
100	0.9232	1.0316	1.0417	0.8658	1.8728	0.636	1.0061
200	0.9353	1.0346	1.0463	0.9102	1.8937	0.662	1.0115
300	0.9500	1.0400	1.0538	0.9487	1.9192	0.687	1.0191
400	0.9651	1.0475	1.0634	0.9826	1.9477	0.708	1.0283
500	0.9793	1.0567	1.0748	1.0128	1.9778	0.724	1.0387
600	0.9927	1.0668	1.0861	1.0396	2.0092	0.737	1.0496
700	1.0048	1.0777	1.0978	1.0639	2.0419	0.754	1.0605
800	1.0157	1.0881	1.1091	1.0852	2.0754	0.762	1.0710
900	1.0258	1.0982	1.1200	1.1045	2.1097	0.775	1.0815
1000	1.0350	1.1078	1.1304	1.1225	2.1436	0.783	1.0907
1100	1.0434	1.1170	1.1401	1.1384	2.1771	0.791	1.0999
1200	1.0509	1.1258	1.4493	1.1530	2.2106	0.795	1.1082
1300	1.0580	1.1342	1.1577	1.1660	2.2429	—	1.1166
1400	1.0647	1.1422	1.1656	1.1782	2.2743	—	1.1242
1500	1.0714	1.1497	1.1731	1.1895	2.3048	—	1.1313
1600	1.0773	1.1564	1.1798	1.1995	2.3346	—	1.1380
1700	1.0831	1.1631	1.1865	1.2091	2.3630	—	1.1443
1800	1.0886	1.1690	1.1924	1.2179	2.3907	—	1.1501
1900	1.0940	1.1748	1.1983	1.2259	2.4166	—	1.1560
2000	1.0990	1.1803	1.2033	1.2334	2.4422	—	1.1610

TABLE VI

Average Mass Heat Capacity of Gases at Constant Volume, c_{vm}, kJ/kg·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	0.6548	0.7352	0.7427	0.6259	1.3980	0.477	0.7164
100	0.6632	0.7365	0.7448	0.6770	1.4114	0.507	0.7193
200	0.6753	0.7394	0.7494	0.7214	1.4323	0.532	0.7243
300	0.6900	0.7448	0.7570	0.7599	1.4574	0.557	0.7319
400	0.7051	0.7524	0.7666	0.7938	1.4863	0.578	0.7415
500	0.7193	0.7616	0.7775	0.8240	1.5160	0.595	0.7519
600	0.7827	0.7716	0.7892	0.8508	1.5474	0.607	0.7624
700	0.7448	0.7821	0.8009	0.8746	1.5805	0.624	0.7733
800	0.7557	0.7926	0.8122	0.8964	1.6140	0.632	0.7842
900	0.7658	0.8030	0.8231	0.9157	1.6483	0.645	0.7942
1000	0.7750	0.8127	0.8336	0.9332	1.6823	0.653	0.8039
1100	0.7834	0.8219	0.8432	0.9496	1.7158	0.662	0.8127
1200	0.7913	0.8307	0.8566	0.9638	1.7488	0.666	0.8215
1300	0.7984	0.8390	0.8608	0.9772	1.7815	—	0.8294
1400	0.8051	0.8470	0.8688	0.9893	1.8129	—	0.8369
1500	0.8114	0.8541	0.8763	1.0006	1.8434	—	0.8441
1600	0.8173	0.8612	0.8830	1.0107	1.8728	—	0.8508
1700	0.8231	0.8675	0.8893	1.0203	1.9016	—	0.8570
1800	0.8286	0.8738	0.8956	1.0291	1.9293	—	0.8633
1900	0.8340	0.8792	0.9014	1.0371	1.9552	—	0.8688
2000	0.8390	0.8847	0.9064	1.0446	1.9804	—	0.8742

TABLE VII

Average Volume Heat Capacity of Gases at Constant Pressure, c'_{pm}, kJ/m³·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	1.3059	1.2946	1.2992	1.5998	1.493	1.733	1.2971
100	1.3176	1.2958	1.3017	1.7003	1.502	1.813	1.3004
200	1.3352	1.2996	1.3071	1.7873	1.5223	1.888	1.3071
300	1.3561	1.3067	1.3167	1.8627	1.5424	1.955	1.3172
400	1.3775	1.3163	1.3289	1.9297	1.5654	2.018	1.3289
500	1.3980	1.3276	1.3427	1.9887	1.5897	2.068	1.3427
600	1.4168	1.3402	1.3574	2.0411	1.6148	2.114	1.3565
700	1.4344	1.3536	1.3720	2.0884	1.6412	2.152	1.3708
800	1.4499	1.3670	1.3862	2.1311	1.6680	2.181	1.3842
900	1.4645	1.3796	1.3396	2.1692	1.6957	2.215	1.3976

TABLE VII *(concluded)*

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
1000	1.4775	1.3917	1.4126	2.2035	1.7229	2.236	1.4097
1100	1.4892	1.4034	1.4248	2.2349	1.7501	2.261	1.4214
1200	1.5005	1.4143	1.4361	2.2638	1.7769	2.278	1.4327
1300	1.5106	1.4252	1.4465	2.2898	1.8028	—	1.4432
1400	1.5202	1.4348	1.4566	2.3136	1.8280	—	1.4528
1500	1.5294	1.4440	1.4658	2.3354	1.8527	—	1.4620
1600	1.5378	1.4528	1.4746	2.3555	1.8761	—	1.4708
1700	1.5462	1.4612	1.4825	2.3743	1.8996	—	1.4867
1800	1.5541	1.4687	1.4901	2.3915	1.9213	—	1.4867
1900	1.5617	1.4758	1.4972	2.4074	1.9423	—	1.4939
2000	1.5692	1.4825	1.5039	2.4221	1.9628	—	1.5010

TABLE VIII

Average Volume Heat Capacity of Gases at Constant Volume, c'_{vm}, kJ/m³·deg

t, °C	O_2	N_2	CO	CO_2	H_2O	SO_2	Air (absolutely dry)
0	0.9349	0.9236	0.9282	1.2288	1.1237	1.361	0.9261
100	0.9466	0.9249	0.9307	1.3293	1.1342	1.440	0.9295
200	0.9642	0.9286	0.9362	1.4164	1.1514	1.516	0.9362
300	0.9852	0.9357	0.9458	1.4918	1.1715	1.587	0.9462
400	1.0065	0.9454	0.9579	1.5587	1.1945	1.645	0.9579
500	1.0270	0.9567	0.9718	1.6178	1.2188	1.700	0.9718
600	1.0459	0.9692	0.9864	1.6701	1.2439	1.742	0.9856
700	1.0634	0.9826	1.0011	1.7174	1.2703	1.779	0.9998
800	1.0789	0.9960	1.0153	1.7601	1.2971	1.813	1.0132
900	1.0936	1.0086	1.0287	1.7982	1.3247	1.842	1.0262
1000	1.1066	1.0207	1.0417	1.8326	1.3519	1.867	1.0387
1100	1.1183	1.0325	1.0538	1.8640	1.3791	1.888	1.0505
1200	1.1296	1.0434	1.0651	1.8929	1.4059	1.905	1.0618
1300	1.1396	1.0542	1.0756	1.9188	1.4319	—	1.0722
1400	1.1493	1.0639	1.0856	1.9427	1.4570	—	1.0819
1500	1.1585	1.0731	1.0948	1.9644	1.4817	—	1.0911
1600	1.1669	1.0819	1.1036	1.9845	1.5052	—	1.0999
1700	1.1752	1.0902	1.1116	2.0034	1.5286	—	1.1078
1800	1.1832	1.0978	1.1191	2.0205	1.5504	—	1.1158
1900	1.1907	1.1049	1.1262	2.0365	1.5713	—	1.1229
2000	1.1978	1.1116	1.1329	2.0511	1.5918	—	1.1296

TABLE IX

Superheated Steam Measured from the Saturation Temperature, c_{pm}, kJ/m³·deg

T, K / p, bar	393	433	473	533	573	593	633	673	733	773	833	873
0.980 66	2.043	1.993	1.985	1.985	1.989	1.993	1.997	2.006	2.022	2.031	2.047	2.060
9.806 6	—	—	2.416	2.294	2.261	2.244	2.219	2.206	2.194	2.190	2.190	2.194
19.61	—	—	—	2.621	2.525	2.487	2.424	2.378	2.341	2.324	2.307	2.299
29.42	—	—	—	2.968	2.801	2.734	2.634	2.558	2.487	2.454	2.416	3.399
39.23	—	—	—	3.483	3.136	3.027	2.851	2.742	2.634	2.579	2.525	2.499
49.03	—	—	—	—	3.467	3.299	3.090	2.931	2.776	2.705	2.633	2.596
58.84	—	—	—	—	3.848	3.655	3.345	3.128	2.927	2.834	2.738	2.692
78.45	—	—	—	—	5.054	4.563	3.948	3.580	3.253	3.115	2.964	2.893
98.07	—	—	—	—	—	5.719	4.719	4.111	3.622	3.421	3.207	3.111
117.68	—	—	—	—	—	—	5.694	4.773	4.048	3.764	3.479	3.345
137.29	—	—	—	—	—	—	7.192	5.593	4.547	4.162	3.781	3.605
156.91	—	—	—	—	—	—	9.659	6.716	5.158	4.631	4.128	3.902
176.52	—	—	—	—	—	—	—	8.336	5.949	5.221	4.555	4.262
196.13	—	—	—	—	—	—	—	11.007	7.063	6.016	5.112	4.727
215.75	—	—	—	—	—	—	—	17.212	9.140	7.453	6.092	5.535

TABLE X **Physical Properties of Dry Air at a Pressure of 101 325 N/m²**

T, K	ϱ kg/m³	c_p kJ/kg·deg	$\lambda \times 10^2$ W/m·deg	$a \times 10^2$ m²/h	$\mu \times 10^6$ N·s/m²	$\nu \times 10^6$ m²/s	Pr
263	1.342	1.009	2.361	6.28	1.67	12.43	0.712
273	1.293	1.005	2.442	6.77	1.72	13.28	0.707
283	1.247	1.005	2.512	7.22	1.77	14.16	0.705
293	1.205	1.005	2.593	7.71	1.81	15.06	0.703
303	1.165	1.005	2.675	8.23	1.86	16.00	0.701
313	1.128	1.005	2.756	8.75	1.91	16.96	0.699
323	1.093	1.005	2.826	9.26	1.96	17.95	0.698
333	1.060	1.005	2.896	9.79	2.01	18.97	0.696
343	1.029	1.009	2.966	10.28	2.06	20.02	0.694
353	1.000	1.009	2.047	10.87	2.11	21.09	0.692
363	0.972	1.009	3.128	11.48	2.15	22.10	0.690
373	0.946	1.009	3.210	12.11	2.19	23.13	0.688
393	0.898	1.009	3.338	13.26	2.29	25.45	0.686
413	0.854	1.013	3.489	14.52	2.37	27.80	0.684
433	0.815	1.017	3.640	15.80	2.45	30.09	0.682
453	0.779	1.021	3.780	17.10	2.53	32.49	0.681
473	0.746	1.026	3.931	18.49	2.60	34.85	0.680
523	0.674	1.038	4.268	21.96	2.74	40.61	0.677
573	0.615	1.047	4.606	25.76	2.97	48.33	0.674

TABLE XI **Physical Properties of Water on the Saturation Line**

T, K	p bar/cm³	c_p kJ/kg·deg	λ W/m·deg	$a \times 10^4$ m²/h	$\mu \times 10^6$ N·s/m²	$\nu \times 10^6$ m²/s	Pr
273	0.006 108	4.212	0.551	4.71	178.8	1.789	13.67
283	0.012 271	4.191	0.575	4.94	130.5	1.306	9.52
293	0.023 37	4.183	0.599	5.16	100.4	1.006	7.02
303	0.042 41	4.174	0.618	5.35	80.1	0.805	5.42
313	0.073 75	4.174	0.634	5.51	65.3	0.659	4.31
323	0.123 35	4.174	0.648	5.65	54.9	0.556	3.54
333	0.199 2	4.178	0.659	5.78	47.0	0.478	2.98
343	0.311 6	4.187	0.668	5.87	40.60	0.415	2.55
353	0.473 6	4.195	0.675	5.96	35.5	0.365	2.21
363	0.701 1	4.208	0.680	6.03	31.5	0.326	1.95
373	1.013 2	4.220	0.683	6.08	28.2	0.295	1.75
383	1.432 7	4.233	0.685	6.13	25.9	0.272	1.60
393	1.985 4	4.250	0.686	6.16	23.7	0.252	1.47
403	2.701 1	4.266	0.686	6.19	21.8	0.233	1.36
413	3.614	4.287	0.685	6.21	20.1	0.217	1.26
423	4.760	4.312	0.684	6.22	18.6	0.203	1.17
433	6.180	4.346	0.683	6.23	17.4	0.191	1.10
443	7.920	4.379	0.679	6.22	16.3	0.181	1.05

TABLE XI *(concluded)*

T, K	p, bar/cm³	c_p, kJ/kg·deg	λ, W/m·deg	$a\times10^4$, m²/h	$\mu\times10^5$, N·s/m²	$\nu\times10^6$, m²/s	Pr
453	10.027	4.417	0.675	6.20	15.3	0.173	1.00
463	12.553	4.459	0.670	6.17	14.4	0.165	0.96
473	15.550	4.505	0.663	6.14	13.6	0.158	0.93
493	23.202	4.614	0.645	5.99	12.5	0.148	0.89
513	33.480	4.756	0.628	5.84	11.5	0.141	0.87
533	46.94	4.949	0.605	5.61	10.6	0.135	0.87
553	64.19	5.229	0.575	5.27	9.8	0.131	0.90
573	85.92	5.736	0.540	4.75	9.1	0.128	0.97
593	112.90	6.473	0.506	4.15	8.5	0.128	1.11
613	146.08	8.163	0.457	3.30	7.7	0.127	1.39
633	186.74	13.984	0.395	1.93	6.7	0.126	2.35

TABLE XII **Physical Properties of Mercury and Some Liquid Metals**

Metal	T, K	ϱ, kg/m³	λ, W/m··deg	c, kJ/kg··deg	$a\times10^2$ m²/h	$\nu\times10^8$ m²/s	Pr$\times10^2$
Mercury Hg:	293	13 550	7.9	0.139	1.57	11.4	2.72
T_f = 234.25 K	373	13 350	9.0	0.137	1.76	9.4	1.92
T_b = 630 K	423	13 230	9.7	0.137	1.91	8.6	1.62
r_f = 11.7 kJ/kg	473	13 120	10.4	0.137	2.06	8.0	1.40
r_{ev} = 291.8 kJ/kg	573	12 880	11.8	0.137	2.39	7.1	1.07
Tin Sn:	523	6 980	34.1	0.255	6.90	27.0	1.41
T_f = 505 K	573	6 940	33.7	0.255	6.85	24.0	1.26
T_b = 2543 K							
r_f = 58.2 kJ/kg	673	6 865	33.2	0.255	6.80	20.0	1.06
r_{ev} = 3015 kJ/kg	773	6 790	32.6	0.255	6.75	17.3	0.92
Bismuth Bi:	573	10 030	13.0	0.151	3.1	17.1	1.98
T_f = 544 K	673	9 910	14.4	0.151	3.5	14.2	1.46
T_b = 1750 K							
r_f = 49 kJ/kg	773	9 785	15.8	0.151	3.9	12.2	1.13
r_{ev} = 855 kJ/kg	873	9 660	17.2	0.151	4.3	10.8	0.91
Lithium Li:	473	515	37.2	4.19	6.2	111.0	6.43
T_f = 452 K							
T_b = 1590 K	573	505	39.0	4.19	6.6	92.7	5.03
r_f = 662 kJ/kg	673	495	41.9	4.19	7.3	81.7	4.04
r_{ev} = 19 594 kJ/kg	773	484	45.4	4.19	8.1	73.4	3.28
Sodium Na:	423	916	85	1.357	24.6	59.4	0.87
T_f = 371 K	473	903	81	1.327	24.4	50.6	0.75
T_b = 1156 K	573	878	71	1.281	22.7	39.4	0.63
r_f = 113 kJ/kg	673	854	64	1.273	21.2	33.0	0.56
r_{ev} = 4208 kJ/kg	773	829	57	1.273	19.5	28.9	0.53

TABLE XIII

Enthalpy, Entropy and Internal Energy of Gases

t, °C	Air			O_2			H_2		
	i	s	u	i	s	u	i	s	u
0	0	0	0	0	0	0	0	0	0
100	100.6	0.3128	71.9	92.32	0.2826	66.2	1 435	4.388	1 022
200	202.3	0.5543	144.8	187.5	0.5083	134.9	2 884	7.838	2 056
300	305.7	0.7524	219.5	285.0	0.6958	206.8	4 333	10.62	3 095
400	411.3	0.9224	296.4	386.0	0.8583	281.9	5 790	12.96	4 138
500	519.6	1.071	375.7	489.4	1.002	359.5	7 256	14.99	5 188
600	629.7	1.206	457.4	595.8	1.131	439.4	8 725	16.78	6 246
700	742.3	1.328	541.2	703.4	1.247	521.2	10 212	18.39	7 320
800	856.6	1.440	627.1	812.7	1.354	604.5	11 715	19.86	8 410
900	973.4	1.544	714.6	923.2	1.453	689.2	13 234	21.21	9 519
1000	1091	1.640	803.7	1035	1.544	774.8	14 775	22.48	10 649
1100	1210	1.730	894.1	1148	1.630	861.6	16 337	23.65	12 800
1200	1330	1.815	985.7	1261	1.709	949.2	17 920	24.77	12 971
1300	1452	1.893	1078.3	1375	1.784	1037.6	19 531	25.83	14 164
1400	1574	1.969	1171.8	1491	1.856	1126.8	21 156	26.83	15 379
1500	1697	2.041	1266.2	1607	1.928	1216.8	22 801	27.78	16 615

Note: Designation and units: enthalpy—i, kJ/kg; entropy—s, kJ/kg·deg; internal energy—u, kJ/kg.

N_2			CO			CO_2		
i	*s*	*u*	*i*	*s*	*u*	*i*	*s*	*u*
0	0	0	0	0	0	0	0	0
103.2	0.3215	80.8	104.2	0.3249	74.5	86.58	0.2692	67.9
206.9	0.5681	155.0	209.3	0.5744	150.0	182.0	0.4957	144.7
312.0	0.7695	230.4	316.1	0.7792	227.1	284.6	0.6921	228.7
419.1	0.9416	307.8	425.4	0.9550	306.7	393.1	0.8662	318.6
528.4	1.093	387.8	537.6	1.110	388.9	506.6	1.023	413.5
640.2	1.229	470.0	651.5	1.249	473.8	623.8	1.166	512.4
754.5	1.352	554.6	768.8	1.376	561.0	744.8	1.297	614.7
870.4	1.466	650.9	887.2	1.492	650.2	868.3	1.418	720.1
988.5	1.571	729.1	1008	1.599	741.3	993.9	1.530	827.7
1108	1.671	818.8	1130	1.699	834.0	1122	1.635	937.5
1229	1.761	910.3	1254	1.793	928.1	1252	1.733	1049.0
1351	1.846	1002.8	1379	1.881	1023.4	1384	1.825	1162.1
1475	1.927	1096.6	1505	1.964	1119.7	1516	1.913	1276.5
1599	2.004	1191.0	1632	2.042	1216.8	1650	1.995	1392.1
1725	2.077	1286.3	1760	2.116	1314.8	1784	2.073	1508.7

TABLE XIV

Average Heat Capacity of Gases in the 0 to 1500 °C Range (linear dependence)

Gas	Mass heat capacity, c_{xm}, kJ/kg·deg	Volume heat capacity, c'_{xm}, kJ/m³·deg
Air	$c_{vm}=0.7088+0.000\,093\ t$	$c'_{vm}=0.9157+0.000\,120\,1\ t$
	$c_{pm}=0.9956+0.000\,093\ t$	$c'_{pm}=1.287+0.000\,120\,1\ t$
H_2	$c_{vm}=10.12+0.000\,594\,5\ t$	$c'_{vm}=0.9094+0.000\,052\,3\ t$
	$c_{pm}=14.33+0.000\,594\,5\ t$	$c'_{pm}=1.28+0.000\,052\,3\ t$
N_2	$c_{vm}=0.7304+0.000\,089\,55\ t$	$c'_{vm}=0.9131+0.000\,110\,7\ t$
	$c_{pm}=1.032+0.000\,089\,55\ t$	$c'_{pm}=1.306+0.000\,110\,7\ t$
O_2	$c_{vm}=0.6594+0.000\,106\,5\ t$	$c'_{vm}=0.943+0.000\,157\,7\ t$
	$c_{pm}=0.919+0.000\,106\,5\ t$	$c'_{pm}=1.313+0.000\,157\,7\ t$
CO	$c_{vm}=0.7331+0.000\,096\,81\ t$	$c'_{vm}=0.9173+0.000\,121\ t$
	$c_{pm}=1.035+0.000\,096\,81\ t$	$c'_{pm}=1.291+0.000\,121\ t$
H_2O	$c_{vm}=1.372+0.000\,311\,1\ t$	$c'_{vm}=1.102+0.000\,249\,8\ t$
	$c_{pm}=1.833+0.000\,311\,1\ t$	$c'_{pm}=1.473+0.000\,249\,8\ t$
CO_2	$c_{vm}=0.6837+0.000\,240\,6\ t$	$c'_{vm}=1.3423+0.000\,472\,3\ t$
	$c_{pm}=0.8725+0.000\,240\,6\ t$	$c'_{pm}=1.7132+0.000\,472\,3\ t$

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